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**Air Quality
Monitoring on
Spacecraft by
Open-Path Fourier
Transform Infrared
(OP-FTIR)
Spectroscopy**

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Executive Summary

Some key characteristics and capabilities of open-path Fourier transform infrared (OP-FTIR) spectrometry were evaluated for potential application of the measurement of trace contaminants in spacecraft air systems. A thorough discussion of wavelength dispersive infrared spectroscopy is given, followed by a detailed description of Fourier transform infrared spectrometry (a multiplexing technique). A description of the monitoring configuration employing open-path FTIR monitoring is given. An overall technology assessment and the areas of the assessment are detailed. The general applicability of OP-FTIR was shown by documenting several studies in similar areas and for similar suites of compounds. Areas that were reviewed include indoor air monitoring for industrial hygiene applications; environmental analysis and fence line monitoring; and the study of planetary atmospheres to show the ability to fly the instrumentation.

The applicability of the OP-FTIR monitoring technique to NASA's target list of compounds was investigated. The target list of compounds are those with spacecraft maximum allowable concentrations (SMACs), which were established for various time limits by NASA for 198 compounds. The SMAC list and the target exposure levels are given in the appendices. The applicability was examined using a commercially available infrared spectral library which contained spectra for 111 of the 198 compounds on the NASA target list. The optimum peak for monitoring and the optimum pathlength ranges for each peak were established for the 111 compounds. Two pathlengths were recommended to assure that most compounds would be observed. A description of compound specificity and the use of open-path vs. closed-cell monitoring is given.

Data reduction methods are required for the quantitative analysis of many compounds simultaneously. The types of data reduction algorithms available and the applicability of these algorithms to multianalyte spectroscopic data is described. The specific hardware and instrumentation needs for this application are discussed and compared to the commercially available and recommended hardware. A description of how the system is envisioned to function onboard the spacecraft is given and the logical sequence of a detection scheme is detailed. In summary, the results and conclusions of the project are given and future studies are suggested.

It was concluded that the open-path Fourier transform infrared monitoring technique is valuable for many reasons. The sensor requires no sample preparation or component separations. The compositional information about the environment is obtained along a path rather than at a sampling point, therefore, the information obtained represents the area rather than a point. The OP-FTIR sensing methodology measures and quantitates ambient air composition in real-time, offers high sensitivity, and detection is compound-specific.

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1.0 Introduction and Objectives

The project outlined in this report was funded by the National Aeronautics and Space Administration (NASA) under contract NASW-96002 and was completed by Melissa D. Tucker, Ph.D., Rebecca C. Rowe, Ellen V. Miseo, Ph.D. and James R. Valentine of Arthur D. Little, Inc. The objective of this project was to investigate the unique capability of long-path and open-path Fourier transform infrared (FTIR) spectroscopy to measure trace contaminants in the air environments of life support systems. This project represents the initial step in an air monitoring systems development program which would transition to the development of instrumentation and data analysis subsystems designed to meet the specific needs of various NASA missions. The project is integral to the requirements for life support monitoring in NASA's efforts to achieve manned space travel for the planned longer missions in the future.

Monitoring the atmosphere onboard spacecraft for chemical contaminants and changes in the concentrations of naturally occurring compounds is required for advanced exploration and long duration space missions and is an ongoing analytical challenge. Spacecraft maximum allowable concentrations (SMACs)⁽¹⁾ have been established for 198 key atmospheric species. NASA has established a program to develop ambient air monitoring sensors to meet the monitoring requirements for advanced exploration of planetary habitats. The air monitoring sensors are intended to be a complete system for identifying, measuring and reporting quantitative results for specified contaminant materials at their respective SMAC exposure level. The immediate need is for reliable measurements of atmospheric constituents. This need is constrained by minimal physical space, minimal available power, a stringent ruggedness requirement, requirement for high reliability and a need for minimal crew attention. It is advantageous to minimize the extent of sampling required so that the monitoring system is simple, rugged, thorough, and reliable.

This study examines the feasibility of using FTIR spectrometry as a sensing methodology to satisfy the monitoring needs for this application. The specific type of FTIR monitoring examined is an open-path sampling methodology, selected because it most closely matches the requirements

The original objectives of the study as it was proposed were to:

- Demonstrate, via experimental testing, that long-path FTIR can be used to measure a limited suite of six contaminants at or below SMAC exposure levels;
- Define data reduction algorithms which can be applied and automated for the quantitation of the contaminants in the suite; and
- Define an FTIR monitoring system which could be used in a subsequent demonstration experiment.

The work was proposed as a series of six tasks:

Task 1 - Obtain a spectral database on a suite of six compounds selected from the SMAC list of target compounds,

Task 2 - Select a pathlength to best achieve quantitative measurement at or below the SMAC level,

Task 3 - Measure quantitative response limits alone and incorporated into any area of interest and provide real-time or near real-time analysis of chemical contaminants in mixtures,

Task 4 - Examine measurement and instrument tradeoffs,

Task 5 - Select test system instrumentation for subsequent demonstration, and

Task 6 - Prepare the final report.

Following award of the contract, we located and ultimately procured a database of vapor phase FTIR spectra, which are in digitized form. The spectral library, "Quantitative Reference Spectra for Gas Analysis," was prepared by Infrared Associates, Inc. (Anaheim, CA). These infrared spectra proved to be suitable for the same purposes as was proposed for our experimentally generated data (in Tasks 1 through 3, above), which was to show feasibility of the proposed methodology. Of even more significance, the database contains spectra for 111 of the 198 compounds (56%) for which SMAC exposure values exist. Thus, the commercially available spectral database allows more extensive coverage of the SMAC compounds than was originally proposed (six compounds) and more useful information for this initial evaluation of the applicability of FTIR.

Access to this larger spectral database enabled us to transfer the effort, which was to have been devoted to the experimental data collection in the proposed effort, to a more extensive analysis of the spectral properties of the SMAC compounds. We have evaluated the major infrared (IR) absorption regions for the 111 compounds in the spectral library (which includes representatives in all but one of the classes of compounds on the SMAC list). In addition, we are investigating the extent of expected interference from water and carbon dioxide with compounds on the SMAC list. These efforts are essential in order to determine the appropriate pathlength(s) for monitoring.

In addition to data analysis requirements, NASA has unique data collection system requirements. The requirements for the data collection system were examined in this project, and a portion of the project was to define the instrumentation and integrated system requirements and to assess the relative importance of the requirements.

This project provides the foundations for a passive, adaptable, area monitor for air quality. The system should be designed so that it can be incorporated into any spacecraft of interest and should provide real-time or near real-time analysis of chemical

contaminants. The focus of the project has been examining the ability of open-path Fourier transform infrared (OP-FTIR) to monitor compounds at or above their SMAC exposure limit for various exposure times. Some preliminary results of this study were presented at the Society of Automotive Engineers, Inc. meeting⁽²⁾.

2.0 Background of Infrared (IR) Spectroscopy Techniques

Brief descriptions of general infrared and Fourier transform infrared spectrometry as well as open-path sampling are provided as a background to the discussion of the applicability of the technique to satisfy NASA's needs.

2.1 Infrared Spectroscopy

Infrared (IR) spectroscopy is a mature technology which has been used by NASA to meet a variety of detection and identification needs. IR is especially useful when a unique chemical signature as a spectrum of the IR absorption (or emission) from molecules of interest can be viewed by a spectrometer as a spectrum. A spectrum is a plot of absorbance as a function of frequency or wavelength. These chemical signature applications are differentiated from the detection and identification of purely thermal signatures emitted by objects at temperatures different from their background. Progress in both instrumental design and data handling now make use of IR as an ambient air monitoring sensor practical.

IR has been used since its inception for both identification and quantitation of a variety of materials, including gas phase molecules. Most organic and many inorganic compounds have distinct infrared signatures and can be identified by these signatures. In addition, after instrument calibration, compounds can be quantified by measuring the absorption or emission of radiation. The instrumentation for these measurements has been used widely in laboratory, indoor and outdoor applications for the quantitative analysis of gaseous compounds in industrial and atmospheric science applications.

Until the mid 1970s, infrared spectral data were acquired primarily using wavelength dispersive spectrometers. In such "conventional IR" measurements, spectral data (i.e., the transmittance of IR energy in a known spectral region defined by frequency or wavelength) is separated into resolution elements by a wavelength dispersing element (a grating or a prism) and collected over a period of time. Each resolution element of the spectrum is measured individually; either simultaneously by several detectors in a polychromator or sequentially by a single detector in a scanning monochromator⁽³⁾. A conventional "spectrum" is then the graphical record of the transmittance (or absorbance) as a function of the frequency (or wavelength) of measurement. A typical spectrum of the atmosphere (containing water vapor and carbon dioxide) is shown in Figure 1.

In IR spectral absorption measurements, molecules are characterized and measured by observing the IR radiation transmitted to a detector from a broadband emitter source when the molecules are "placed" in the region between them. Any molecule contained in the line-of-sight path between the source and the detector is observed if it absorbs infrared energy. Because the measurement is made of all molecules between the source and detector, the monitoring technique is referred to as path-averaged. The resulting IR spectrum is representative of the entire data collection time and the entire path between

the source and the detector. A cell of known pathlength is usually used to contain the sample observed during studies of fluid phase (either gas or liquid) samples.

Spectral absorption by infrared active molecules is governed by the general absorption spectrometry relationship called Beer's Law, which states that the relationship between absorbance and concentration is: $A = abc$ (A = absorbance, a = absorption coefficient, b = pathlength and c = concentration). Absorbance is derived from the transmittance (extent of transmission) of the radiation in the presence or absence of the absorbing molecules [i. e., $A = -\log(T_{\text{with sample}}/T_{\text{without sample}})$]. Thus, the absorbance at each frequency is governed by the absorption coefficients at each frequency and the concentrations of the individual molecular species present along a known path length. In more general terms, the extent of absorbance is described by the absorption coefficient and the number of molecules present in the path.

Spectral absorbances appear as peaks; there is an absorbance of maximum intensity with less intense absorbances surrounding it. Therefore, the presence of a compound may be determined by the peak center location and the overall peak shape. In addition, most compounds have more than one peak within a given spectral window. This combination of absorbance features makes identification of compounds very accurate. Because no two compounds have identical peaks in all the same spectral locations, this accuracy leads to compound-specific identification.

Spectral data may be analyzed manually or using computerized algorithms to perform data analysis. The term data analysis generally refers to the process of extracting information from data. In spectroscopy, data analysis is finding the optimum wavelength or wavelengths for analysis and generating the most accurate and robust calibration to relate the set of spectroscopic data to a reference set of calibration spectroscopic data. For data observed on spacecraft, computerized algorithms should be used for most data analyses to maximize efficiency and speed. In the specific event of ambiguous results, manual analysis by a trained scientist may be used as a confirmatory methodology. This topic will be discussed in further detail in this document.

The frequency range used for measurement of organic molecules is 4000 to 500 cm^{-1} (the so-called "mid-infrared" range). The presence of atmospheric water vapor and carbon dioxide limit the areas of the mid-infrared spectrum that can be used for air analysis, but spectral "windows" or regions of wavenumbers containing no atmospheric absorbances are seen at roughly $700\text{--}1300\text{ cm}^{-1}$, $2000\text{--}2250\text{ cm}^{-1}$ and $2400\text{--}3000\text{ cm}^{-1}$ ⁽⁴⁾. These spectral "windows" can be seen in the atmospheric absorption spectrum in Figure 1. Analysis of multiple components in a gaseous mixture can be easily accomplished if an isolated peak can be found for each compound or if some type of chemometric data analysis is used to separate the contributions from overlapping peaks⁽⁵⁻¹⁰⁾.

Despite the limitations of the available spectral "windows" noted above, IR is particularly appropriate for ambient air monitoring. The inherent specificity and sensitivity of the monitoring approach will afford both identification and quantification of a variety of compounds without sample preparation. The high speed of spectral

measurement and data processing allows rapid response to the presence (or absence) of compounds in the spacecraft environment. The sensitivity of the instrument should permit detection of most compounds at or below their SMAC limit. The instrumentation has been made both rugged and simple for easy operation and maintenance.

2.2 Fourier Transform Infrared Spectrometry

A different approach to obtaining spectral information utilizes a multiplex analyzer that collects spectral data about the intensities of all the wavelengths simultaneously using a technique known as interferometry. The information is not separated according to frequency resolution element, but is encoded in time by the interferometer to yield an interferogram of the sample. The information in the interferogram can be decoded mathematically by applying a Fourier transform (FT) to yield the same information in the desired frequency format or spectrum.

The multiplex technique is based on the interferometer originally designed by Michelson in 1891⁽¹¹⁾. An infrared spectrometer which uses the approach is referred to as a Fourier transform infrared (FTIR) spectrometer because it relies on a Fourier transform to obtain spectral information about molecules (in the frequency domain) from the interferograms collected by the instrument (in the time domain). Though the relationship between the time and frequency domains via the Fourier transform was discovered over one hundred years ago, FTIR spectrometers did not become commercially available until the late 1960s with the development of modern computers and the advancement of electronics.

Michelson interferometers contain a beamsplitter in which light, passing from an infrared source, is split into two optical beams. Each beam strikes a mirror and the beams are recombined and sent to the detector. One mirror is stationary and the other mirror moves. When the mirrors are the same distance from the beamsplitter, there is complete constructive interference. The greater the difference in the path (called the optical path difference), the greater the destructive interference. The intensity variations of the beam emerging from the interferometer can be measured as a function of path difference or time by a detector. The detector output (electric current) has a constant (dc) component and a modulated (ac) component. Only the ac component is important in spectrometric measurements and it is this modulated component (or a plot of same) that is generally referred to as the interferogram. Data in an interferogram format is referred to as being in the time domain and the point of complete constructive interference is called the ZPD for zero path difference. Interferometers collect data in an interferogram format, and a subsequent mathematical (Fourier) transform operation on the interferometric data are needed to obtain the more familiar spectral data.

Three of the primary advantages gained when employing Fourier transform instead of wavelength dispersive spectrometers are the Fellgett's (multiplex) advantage, the Jaquinot (throughput) advantage, and the Conne's (wavenumber precision) advantage. The Fellgett's or multiplexing advantage is realized when collecting time domain data because, unlike wavelength dispersive spectrometers, all the frequencies in the spectrum are recorded all the time. Therefore, the time to collect a comparable spectrum with an

FT instrument is much shorter than with a wavelength dispersive instrument. The computation of the FT is essentially instantaneous because many efficient algorithms have been written and computers are sufficiently fast. In cases where speed of computation is essential, digital signal processors devoted to the FT are employed.

Throughput measures the relative amount of incident light transmitted through the aperture on the instrument. The Jaquinot, or throughput, advantage is realized in a multiplexing instrument because a greater proportion of the source radiation passes through the instrument than does with a wavelength dispersive instrument. The reason for this is that the interferometer uses a circular entrance aperture larger than the slit area for a wavelength dispersive instrument with the same resolution.

The Connes, or wavenumber precision, advantage is realized in a multiplexing instrument because interferometers incorporate a helium neon (He-Ne) laser to permit the interferogram to be digitized at equal intervals of retardation. The He-Ne laser is carefully aligned to assure wavenumber accuracy and precision. If there is some indication that the He-Ne laser is not aligned correctly, the wavenumbers will still be precise, but not accurate. The shift always varies linearly with wavenumber and the value of the laser wavenumber entered into the transform algorithm may be corrected after calibration and a precise and accurate spectrum calculated.

FTIR offers greater sensitivity, shorter data collection time, a better signal to noise ratio and better spectral resolution when compared to wavelength dispersive spectrometers. These advantages, along with the relatively inexpensive cost of instrumentation, have resulted in virtually complete replacement of dispersive instruments by FTIR in new instrument development and sales over the past few decades.

The minimal components of an FTIR spectrometer are: an interferometer, a detector, a He-Ne tracking laser, electronics and a computer with appropriate software to control the spectrometer system. In addition, an FTIR spectrometer may contain an internal or external source of IR radiation, mirrors, lenses, cells, optics and/or apertures.

2.3 Open-path FTIR Spectrometry

FTIR spectrometry is an established monitoring technique with versatility in monitoring application. It usually entails the use of a sampling cell or some other containment vessel for the sample. Open-path FTIR (OP-FTIR) is essentially the same as conventional FTIR except, although the sample pathlength is known, there are generally no cell walls and movement of airborne substances (vapor or particulate) in and out of the optical path is not constrained. Thus, the compounds between the source and the detector in the open atmosphere are observed.

A typical open-path monitoring system with monostatic source and detector is shown in Figure 2. The FTIR, with infrared source and detector, is housed with some telescoping optics on the appropriate mounting device. A retroreflector is placed at some distance from the FTIR and the optical beam passes from the instrument to the retroreflector, is

reflected, and travels back. The analytes present along the optical path are measured and the spectrum is calculated. In this description of a monostatic sampling configuration, the source and detector are co-located; however, the source and detector could just as easily be located some distance apart. If no retroreflector is used and the source and detector are placed at opposite ends of the sampling configuration, the observation is said to be bistatic. Thus, many optical configurations may be used to achieve the appropriate path to monitor the compounds of interest.

The components to be monitored do not flow through a cell and it is important to monitor in areas where the compounds are most likely to be present. The monitoring is described as area monitoring instead of point monitoring. For example, to determine the quality of breathing air, monitoring should be performed at the height of a typical person. To monitor emissions from automobiles, monitoring should be performed at the height of the tail pipe. If more than one path is likely to contain the compounds of interest, mirrors may be used to divert the optical beam along more than one path to monitor multiple locations. Figures 3(a) and (b) show an open-path monitoring configuration which has two paths: a shorter path and a longer path. The paths are setup by placing retroreflectors in two places and varying the path used for analysis by diverting the beam of infrared energy from the instrument. The path monitored changes as the first mirror is moved from the position in Figure 3a) to the position in 3b). This monitoring configuration allows the system to monitor compounds in different locations and at different concentrations. Multiple passes of the optical beam through the same general space may be done to achieve a longer pathlength over a specific area. This monitoring configuration is shown in Figure 4.

The first use of OP-FTIR was reported by Low⁽¹²⁾ in 1967 to monitor the emissions from the smokestack of an industrial plant. Since the early 1970s, FTIR monitoring has been used for the analysis of atmospheric compounds because of its selectivity, accuracy and quantitative precision for gases^(4, 13, 14). Since that time, the development of computers and the advancement of electronic components has helped to make FTIR systems faster and smaller facilitating the open-path monitoring configuration.

OP-FTIR has been used extensively to monitor pollution and characterize air quality in both indoor and outdoor applications. Typical outdoor applications have been: monitoring pollutants in stack gases^(4, 12, 13), characterization of fugitive emissions⁽¹⁵⁾, air quality monitoring during remediation⁽¹⁶⁾, fence line monitoring⁽¹⁷⁾, and characterization of industrial atmospheres⁽¹⁸⁾. Indoor air monitoring by OP-FTIR has been used to monitor workplace gas and vapor exposures⁽¹⁹⁾, to characterize the air in homes⁽²⁰⁾, and to construct two-dimensional concentration maps using computed tomographic techniques⁽²¹⁾.

3.0 Results and Discussion of the Technology Assessment

The overall assessment of applying OP-FTIR technology to spacecraft monitoring consisted of several individual studies. The feasibility of monitoring for SMAC compounds was examined by assessing the extent and type of work done in related areas in the open literature. Then, spectral libraries were examined to see how well they matched the SMAC list of compounds. The study initially planned to encompass six compounds, but the final study was performed on 111 compounds.

Once one spectral library was selected⁽²²⁾ and examined, it was used to assess the optimum peak for monitoring and the optimum pathlength for analysis of each compound contained in the library that is also on the SMAC list. Then, the type of data reduction algorithms that have been and should be used were examined and described. Commercially available hardware was assessed and the state of the art of the industry was compared to the needs for onboard monitoring.

A description is given of the results obtained during the technology assessment in five sections. The general applicability of FTIR for monitoring atmospheric contaminants is discussed to show the characteristics of FTIR that make it appropriate for this study. The applicability of the sampling methodology to the compounds contained in the SMAC list is discussed. The pathlength requirements to meet SMAC level monitoring needs are calculated and detailed. A discussion of compound specificity and measurement interferences is given. The section is concluded with a discussion of the use of open-path and closed-cell sampling configurations.

3.1 General Applicability of FTIR for Monitoring Atmospheric Contaminants

Considerable development effort has been devoted by the community of infrared spectroscopists and chemometricians to solve multianalyte problems such as the one described by this report. Advances in three distinct technical areas provide appropriate bases for this application of FTIR sensing: industrial hygiene studies of indoor air quality, Earth atmospheric pollution studies, and planetary astronomy. These areas have developed since the 1950s and each has led to developments and modifications of FTIR technology for gaseous measurements.

The area of environmental pollution studies has been reviewed by Hanst⁽²³⁾ while indoor air monitoring applications have been reviewed by Lee, Hood and others⁽²⁴⁾. Fink and Larson⁽²⁵⁾ have reviewed the astronomy applications. Other articles give overviews of the general area of FTIR and its evolution in applications⁽²⁶⁻²⁸⁾.

The study of planetary atmospheres was one of the early applications of field based OP-FTIR spectroscopy. Fellgett⁽²⁹⁾ first demonstrated the feasibility of the technique in 1958 for observing stars. In the decades to follow, FTIR was shown to be a feasible method for studying various atmospheric phenomena in the 1 to 4 micron (10,000 to 2500 cm⁻¹) spectral region^(30, 31). The 5.5 to 50 micron (1818 to 200 cm⁻¹) region was often used in

the laboratory with good results, but not for astronomy applications. Compounds detected by these techniques included HCl and HF in the atmosphere of Venus; CO in the atmosphere of Mars; and ethane, acetylene and GeH₄ in the atmosphere of Jupiter.

In the area of environmental monitoring, FTIR has been used to monitor stack gases using the open-path monitoring configuration^(4, 12, 13) since the late 1960s. In particular, the technology has been used for: the characterization of emissions during the remediation of a gas plant⁽¹⁷⁾, and the analysis of many gaseous mixtures^(7, 8, 32). FTIR has also recently been used as a continuous emissions monitor (CEM) to detect a small suite of analytes particular to the monitoring application^(33,34). CEMs operate in an unattended mode for long periods of time, from several hours to several months.

Recent indoor air monitoring applications have focused on monitoring many compounds simultaneously and using chemometrics to perform the data reduction^(5, 20). In a study by Ying and Levine⁽⁵⁾, gaseous mixtures of two to six compounds with 50, 10, 1 and 0.1 ppm concentrations were studied. Data analysis was performed using the least squares fit (LSF) method. Their findings support the conclusion that the FTIR spectrometer is an appropriate method for direct quantification of multicomponent mixtures of many airborne gases and vapors. In a similar study, four different mixtures of up to 26 compounds at the 2 to 5 ppm concentration range were analyzed⁽⁷⁾. Compound specificity percentages were consistently in the high 90's and sensitivity percentages were in the low 90s. Equations for sensitivity and specificity are given as: sensitivity = true positives / (true positives + false negatives) and specificity = true negatives / (true negatives + false positives).

Many of the characteristics necessary for long-term atmospheric analysis in NASA applications have been proven in other areas, as evidenced by the studies discussed. The environmental applications have shown the use of FTIR to monitor many of the compounds of interest to NASA. The planetary atmospheric studies have shown that the technology can be configured to be used on flight missions. The indoor air monitoring applications most closely mimic the application being investigated. High sensitivity and compound specificity levels have been demonstrated and are expected in development programs. Therefore, there is compelling evidence that FTIR is a viable gas analysis technique for analysis of trace contaminants in air.

3.2 Applicability to SMAC List Compounds

The list of air contaminants for which Spacecraft Maximum Allowable Concentrations currently exist (i.e., the "SMAC" list) is in JSC Report 20584⁽³⁵⁾ and shown in Appendix B of this report. This current SMAC list contains 198 compounds from many chemical classes including inorganic acids, alcohols, aldehydes, aromatic hydrocarbons, chlorocarbons, esters, ethers, ketones, organic acids, and other types of compounds. Maximum allowable exposure limits in parts per million (ppm) are given for one hour, 24 hours, 7 days, 30 days, 180 days, 365 days and 600 days exposures.

Two available collections (libraries) containing digitized FTIR spectra of vapor-phase compounds were examined to determine the number of SMAC list compounds that they contained. These library collections have been developed independently by spectroscopists using different approaches to sample preparation and data collection. The infrared signatures are qualitatively the same, but the quantitative relationship between absorbance and concentration may be different between the libraries. As such, they are considered to be self-consistent for internal quantitative comparison, but may not be as useful for quantitative intercomparison. One library of the two was selected for the continued analysis because it better represented by the compounds on the SMAC list (i.e., it contained more of the compounds distributed across more of the chemical classes in the SMAC list). The spectral library contained 111 of the SMAC compounds distributed across 14 of the 15 chemical classes on the SMAC list. As shown in Figure 5, the selected library contained a good overall representation of the compounds of interest to NASA.

The only class of compounds listed on the SMAC list and not in the selected library was the silicones. There were a total of three silicones listed on the SMAC list. The compounds have distinct infrared signatures and may be selected as initial candidates for the spectral library to be collected as a part of further development efforts. The only compounds on the SMAC list that cannot be observed by FTIR are the homonuclear diatomic molecules hydrogen (H_2) and oxygen (O_2) which do not have IR absorption spectra.

Carbon dioxide (CO_2) is listed on the SMAC list and is a strong infrared absorber. It is a natural product of respiration and hence is always found at some level in the atmosphere of life support systems. While quantitative measurement of CO_2 might be difficult using the FTIR apparatus appropriate for this trace contaminant application because there is a strong CO_2 absorbance (see Figure 1 for example), in fact IR measurement using single wavelength photometry is used as the basis for commercial building ventilation CO_2 monitors. Indeed, we have used a modified version of such a single wavelength monitor (a filter photometer) as the CO_2 monitor in the environmental control system of the Plant Growth Facility (the PGF) which Arthur D. Little, Inc. has built for NASA Kennedy Space Flight Center. This PGF is scheduled for its maiden flight in November 1997 on *the Orbiter*. Thus, while CO_2 is a strong infrared absorber and is in the spectral library, it was not included as a candidate on the various tables. The measurement of trace amounts of species in the presence of percent amount of the same species is not reliable.

For each target compound in the spectral library, the value for absorbance (A) was determined from the absorbance spectrum at a specific frequency. The absorbance value reported is the peak height, which is measured by the maximum peak absorbance minus the baseline absorbance. Tables 1 and 2 list the wavenumber range of the peak used for each compound. Table 1 is listed in alphabetical order by compound and Table 2 is listed in ascending order by maximum peak frequency.

The compounds from the SMAC list often have many other peaks, but one peak was selected for this study. The criteria for peak selection was:

- Minimization of spectral overlap with atmospheric water and carbon dioxide,
- Pathlengths between 1 and 50 meters for monitoring at the SMAC level, and
- Observed detection at the SMAC level.

The peak selected for each compound gives the best overall range of concentrations at or above the SMAC level using a pathlength that is reasonable for the spacecraft application.

3.3 Pathlength Requirements to Meet NASA Needs

Since FTIR is a technique that acquires information along the entire path between the source and the detector, the pathlength can also be varied to change the absorbance - concentration relationship. The path between the source and the detector can be contained in a closed-cell (point source) or open-path (path averaged) configuration. The source and detector may be in the same location with a retroreflector or mirrors in a remote location (Figure 2). The pathlength of analysis is the entire path of the infrared beam between the source and the detector. Pathlengths up to 1000 meters may be achieved by using a multi-pass configuration achieved by placing appropriate optics along the beam⁽³⁶⁾. The beam may be folded up to 20 times (Figure 4). It is important to assure that the optical throughput is sufficient to allow monitoring of the species of interest so the number of mirror reflections should be 20 or fewer.

By placing mirrors in various places within the spacecraft, both long and short paths may be observed within the environment simply by diverting the beam along different paths. An alternative sampling configuration involves using several paths to observe a broad range of concentrations for a compound (Figure 3). In Figure 3a, the beam is directed through a shorter path than in Figure 3b. The beam might also be directed perpendicular or behind the sensor using optical components.

The spatial distribution of compounds within the spacecraft could be determined by using tomographic reconstructions as done by Park, Yost and Levine⁽²⁰⁾. In this study, the path-averaged data from an OP-FTIR system was used to reconstruct two-dimensional concentration maps of the gas and vapor contaminants in workplaces using computed tomographic techniques. The sampling used a fan geometry with 52 flat mirrors placed along the perimeter of the monitored chamber. A single FTIR spectrometer and a single detector were used to monitor the area of a 24 x 21 x 8 foot test room. A total of 195 pixel values were obtained and pixel areas intercepted by the rays for each geometry were calculated. In another geometry, they used 52 flat mirrors and 52 retroreflectors. The reconstructive maps that were generated for the tests show the presence or absence of compounds as a function of compound type, location and time. This work could be done more simply by using fewer mirrors or by using multiple OP-FTIR sensing systems.

For the case of this feasibility study, some assumptions were made. It was assumed that the relationship between absorbance and concentration is linear and that zero concentration corresponds to zero absorbance (i. e., a single spectrum was used to determine the absorbance/concentration relationship). Although this is not recommended for experimental measurements, it is reasonable for drawing conclusions about general method applicability. In more detailed phases of the study, the exact spectral behavior of the target compounds should be assessed by careful calibration. Making these assumptions allowed for a general overview of most of the compounds of interest for a relatively low cost.

The absorbance value used in the pathlength calculations is by definition between zero and one. The absorbance values used to assess the minimum and maximum pathlength were set at 0.005 for the minimum and 0.8 for the maximum. 0.005 absorbance units was selected to be the minimum absorbance and is based on the observation that spectra with atmospheric and other interferences have peak to peak noise levels below 0.001 absorbance units. Three times the peak to peak noise value is often used for detection limit values, but to be certain that any error came on the side of being too conservative a value of five times the peak to peak noise was used as the minimum absorbance value to be observed. Absorbance is fairly linear up to about 0.85 or 0.9 absorbance units and a maximum absorbance value of 0.8 was used for feasibility calculations.

Once the best commercially available library was selected for this study, the pathlength required to monitor each compound at the SMAC level was determined. The variables used in calculations based on Beer's law are spectral absorbance, absorption coefficient, pathlength, and concentration. Since the pathlength is the variable that is unknown in this portion of the study, the form of Beer's law that is used is: $b = A/ac$.

The absorption coefficients used in the pathlength calculations for each compound were calculated from the spectra in the spectral library according to Beer's law ($a = A/bc$). The absorbance is measured from the spectra as the peak maximum absorbance minus the baseline absorbance. The path - concentration product used for each spectrum is given and the absorption coefficient for each compound is determined. A plot of absorbance as a function of the path concentration product yields a line with a slope equal to the absorption coefficient (a). For this calculation, the absorbance value was calculated from the spectrum. The concentration and path used for data collection were given with each spectrum and used in the calculations.

The concentration values used in the calculation of the optimum pathlengths were the SMAC level concentrations for the one-hour and for the 7-day exposure times. These SMAC exposure values are shown in Appendix A as are SMAC limit values for other exposure times⁽³⁵⁾. For the 111 SMAC compounds that are found in the spectral library (excluding CO₂) 8% (9/111) have SMAC data for only 7-day exposure. In addition, 23% have the same SMAC exposure level for all exposure times from one hour to 600 days and 43% of the compounds (48/111) have the same SMAC exposure level from 7 days to 600 days (including 30 days, 180 days, and 365 days).

Once the absorption coefficients were calculated for each compound, Beer's law was used to determine the pathlength required to observe compounds at or above their instrumental limit of detection ($b=A/ac$). Both minimum and maximum pathlength calculations were completed for the one-hour (Tables 3 and 4) and the 7-day (Tables 5 and 6) SMAC exposure limits. The range of pathlengths that will yield an on-scale peak for the SMAC levels are the range of paths between the minimum pathlength and the maximum pathlength shown for each compound in Tables 3 through 6. Tables 3 and 4 are one-hour exposure SMAC data; Table 3 is sorted alphabetically by compound and Table 4 is sorted by the minimum pathlength. Tables 5 and 6 are 7-day exposure SMAC data; Table 5 is sorted alphabetically by compound and Table 6 is sorted by the minimum pathlength.

The pathlengths required for monitoring compounds at each exposure level were determined by finding pathlengths that offer monitoring of each compound while minimizing the number of compounds that cannot be seen either because their SMAC exposure limits are very high and they require very short pathlengths or their SMAC exposure limits are very low and they require very long pathlengths. The minimum number of different pathlengths should be used and optical switching between the mirrors can be used so that one instrument is sufficient for monitoring.

Detection of compounds at the one-hour SMAC exposure levels requires multiple pathlengths. Using a 15 cm and a 25 m pathlength, all but five compounds are detected at or below their SMAC one-hour exposure concentration. This can be observed in Table 4, by looking at pathlengths that lie between the minimum path and the maximum path for the greatest number of compounds. If an additional pathlength of 100 meters is added, three of the five compounds may be observed; however, optical alignment and throughput may be difficulties at this pathlength.

Notice the very high pathlengths for detection at the one-hour SMAC exposure for acrolein and methylhydrazine. The SMAC limits for these compounds for one hour are 0.013 ppm and 0.0021 ppm, respectively. The low limit of detection in this case results in the need for a high pathlength to monitor the compounds. The next highest path requirements is for hydrogen sulfide. The SMAC exposure limit for this compounds is 15 ppm; however, it is not a very good absorber of infrared energy. Therefore, the pathlength required for monitoring the compound must be greater than 96 meters.

Detection of compounds at the 7-day SMAC exposure levels requires multiple pathlengths. If a 0.2-meter (20 cm) path and a 40-meter path were used, all but 7 of the SMAC compounds in the infrared library could be detected at or below their SMAC exposure limit (Table 6). Of the seven remaining compounds: one of the seven would be detected at a 100-meter pathlength, two of the seven would be detected at a 270-meter pathlength, and three of the seven would be detected at a 420-meter pathlength. It might be reasonable to include a 100-meter pathlength, but the importance of the compound (nitrogen dioxide), cost for additional equipment, cost for additional analysis, and impact on the measurement frequency along the other pathlengths should be considered in decisions such as this one.

Of the compounds not observed with a 40-meter pathlength, the 7-day SMAC exposure limits vary from 0.0021 for methylhydrazine to 2.0 for hydrogen sulfide. It is a combination of the detection limit and the inherent strength of infrared absorption that determine the overall pathlength required for analysis.

3.4 Compound Specificity and Measurement Interferences

Infrared spectroscopy is used to collect information about molecules by observing molecular vibrations. Molecules undergo changes in vibrational energy state when subjected to excitation radiation. The source used for FTIR is a broadband source and emits a continuum of radiation energy across the mid-infrared absorbing region ($\sim 400\text{--}4000\text{ cm}^{-1}$, $2.5\text{--}50\text{ }\mu\text{m}$). If a compound has a natural vibration between its constituent elements at a frequency (given in waves per cm or cm^{-1}), it will naturally absorb energy at that wavelength. The exact frequency of the natural vibration results from the elements that are bonded and their environment. One influence on their environment is the elements that surround them in the molecule. Therefore, no two differing molecules have the same exact makeup of vibrations along their bonds. If a molecule has a large portion in common with another compound, they may have portions of their infrared signatures that are similar, but not exactly the same.

The infrared signature consists of one or more peaks which are absorbances in a spectral region. Each peak is a distribution of the energy levels associated with the vibration. Spectral resolution determines if the energy levels are observed as distinct absorbances or if they blend together. For example, when looking at a film of a picket fence on TV, it is easy to distinguish the individual plackets comprising the fence. Your eyes and the pixels on the TV set have ample visual resolution to allow you to observe the plackets of the fence. However, if the plackets of the fence are close together and the TV does not have good resolution (or the fence does not cover a large portion of the TV, if it is in the background of the scene), the fence may appear as a solid item. This may also happen with infrared peaks, if the instrument does not have ample spectral resolution the individual bands within the peak may be blended.

The distribution that the vibrations take varies as does the transform of the distribution which is manifested in the peak shape. Because compounds may have a portion of a peak that overlaps with the portion of a peak from another compound, various measures may be taken to assure that compound identity and amount may be measured. Various scientists have studied this issue of deconvolving or differentiating the contribution of one curve from another in the areas of physics, mathematics, and chemistry.

Because a broad band source is used, absorbances at all frequencies emitted by the source are observed if there are a substantial number of molecules of interest present that the detector can differentiate them from a background signal. If this is the case, we say that the instrument is observing the compound at or above its limit of detection (LOD). Each compound has a unique signature differentiated by peak location, peak shape, presence of multiple peaks, and relative intensity of the multiple peaks.

Peaks from molecular vibrations within different types of molecules may overlap. The overlap may be partial or complete. When molecules partially overlap, they may be differentiated by deconvolution methods which rely on the fact that the peaks are of a known subset of regular distributions (Lorentzian, Gaussian, etc.). The same methodologies are employed when differentiating peaks overlapping, which may occur when a strongly absorbing compound has a vibration in the same general frequency region as a weakly absorbing compound. The peak centers or shapes may not be the same, but the larger peak may cover the smaller peak. The result is a peak that does not have a regular distribution pattern and this can often be determined by a computer. If computational methods are not available, spectral subtraction of a calibration spectrum may be used. The spectrum of the known compound at a known concentration is subtracted from the spectrum with the overlapping peaks. The underlying peak will appear as the contribution of the larger peak is subtracted.

When analyzing infrared spectra a single peak or multiple peaks may be used. When using automated spectral interpretation often assignments are made based on how well a spectrum matches a library spectrum. This pattern recognition methodology uses various algorithms to match the spectra and works well for pure compounds that closely match their library or reference spectra.

When there are spectral interferences or overlaps, a different type of interpretation may be used. These more complex types of data interpretation rely on construction of basis sets of eigenvectors rather than pattern recognition. Therefore, the interpretation methods may be updated as they see more and more spectra.

3.5 Use of Open-path and Closed-cell Sampling Configurations

From the above discussions, it is clear that cell path length is the most important consideration to assure that SMAC compounds may be monitored at their SMAC exposure level. Cell walls are only needed when it is desirable to avoid changes in the substances being measured, either through reaction with or dilution by the surrounding atmosphere. For the application under consideration, the ability to obtain spectral data on the in-situ atmosphere by passing the IR beam through a region which is continuous with the region of interest rather than having to pump the atmosphere through a contained cell is a significant advantage. The open-path configuration is described as an area or volume sampler approach while the closed cell is a point sampler approach.

Since the FTIR technique collects data on all frequencies simultaneously and integrates them over time, any variation in composition during the data collection time will be accounted for in the integration. This time-insensitivity allows the sensor to obtain a general picture of the atmosphere and is a clear advantage of the FTIR technique for this monitoring application.

4.0 Data Reduction Methods and Algorithms

Data analysis refers to the entire process of extracting information from analytical data. Computers enable us to collect enormous amounts of data, which are useful only when they are interpreted (i.e., when data become information). Calibration is the process by which the response of a measurement system is transformed to, or expressed in terms of, a quality or a quantity of interest⁽³⁷⁾. The use of any sensor that acquires data very quickly or over long time frames requires some type of automated data analysis and reporting to deliver real-time information.

Various types of multivariate statistics have been used for calibration and analysis of data to automate interpretation and correlate observations with concentrations or some other physical parameter. Multivariate statistics is a collection of mathematical tools that can be applied to chemical analysis when more than one measurement is acquired for each sample. Some commonly used multivariate statistical techniques are: multiple linear regression (MLR), principal component regression/ analysis (PCR/ PCA), partial least squares (PLS) and classical least squares (CLS). The application of multivariate statistics to chemical systems is called chemometrics.

4.1 Introduction to Data Reduction Algorithms

Chemometric data reduction algorithms have characteristic computational steps: calibration and prediction⁽³⁹⁾. The calibration step begins by constructing a data matrix from the instrumental responses for a given set of calibration samples. The calibration set relates an instrumental response to a physical parameter. An independent referee method is usually used to confirm the physical parameter. The goal of the calibration phase is to produce a model that relates the instrumental response to the values obtained by the referee methodology. The prediction step consists of choosing an appropriate mathematical method that will best reproduce the values obtained by the referee methodology for the given instrumental response.

The classical least squares (CLS) or least squares fit (LSF) method attempts to find a linear model that estimates the values for physical parameters as closely to the known physical parameter (from the referee methodology) as possible. Multiple linear regression (MLR) is a technique that attempts to find a linear combination of variables such that the model estimates the values for physical parameters as closely to the known physical parameter (from the referee methodology) as possible. MLR's criterion is to minimize the sum of the squares of the deviations between the predicted and the true (referee methodology) values. MLR does not attempt to model the underlying structures or factors that may exist in the instrumental data or the data from the referee method (physical data). MLR may, therefore, incorporate significant amounts of information into the model. In general, MLR is a good data reduction scheme for ideal situations. However, MLR may incorporate significant amounts of irrelevant variance (information) into the model.

Principal component regression (PCR) is a factor (or eigenvector) based method. It creates a basis set of eigenvectors and eigenvalues which can be used to represent the instrumental data. The eigenvectors are found in decreasing order of importance. The first principal component or the first eigenvector (which has the greatest eigenvector eigenvalue product) contains the information that best represents the data obtained on the instrument, but ignores the information from the referee method. The first principal component has the smallest error when it is used to estimate the original variables. Additional principal components are found each with increasing error when used alone to estimate the original variables. Ideally, when the principal components are used as a group, they model the instrumental data well. So, although this method is more rigorous than MLR, it does not incorporate the referee method data into the building of the data analysis model.

Partial Least Squares (PLS) is a factor based method that considers both the instrumental measurement and the physical data from the referee methodology. The underlying factors in instrumental response and referee methodology values are determined simultaneously and a prediction of physical data (as you get from a referee method) for instrumental responses is calculated.

There are many other chemometric methods that should be considered during the experimental phase of this method validation. In addition, the optimum data collection parameters should be determined, including: spectral resolution, data collection time and signal averaging times. The amount of data stored should be minimized by, for example, disregarding the information from the spectral regions blocked by CO₂ and water.

4.2 Data Reduction Algorithms for Spectroscopic Systems

Decisions about compound identity and concentration from spectroscopic instrumentation are based on peak location, shape and intensity across a spectral region. Although two peaks may be in the same general spectral region, their shape and intensities may vary. Absorbance information across many wavenumbers is used with a chemometrics algorithm to correlate compound identity and concentration with instrumental response (spectral information).

Conceptually, the term data analysis refers to the entire process of extracting information from data. In spectroscopic analysis, it has a more restricted meaning. In the context of spectroscopy, by performing data analysis we mean finding the optimum wavelengths to generate the most accurate and robust calibration. The calibration relates a given set of spectroscopic data to reference laboratory values for the composition of a set of samples, to be able to analyze future samples of unknown composition. The basic process is the concept of fitting a straight line to data, extended to include the possibility of having more than two variables as input.

The most common method of calibrating spectroscopic instruments is MLR of the absorbance at some number of wavelengths against the reference laboratory values. Regression is the process of mathematically determining the best possible fit of a straight

line to a set of data. The example of a line is appropriate for data in 2 dimensions, in other words data with two coordinates. A two-dimensional data point is mapped in one-dimensional space (a plane) and is fit with a line. If data contains three coordinates (x, y, z), it can be plotted in two-dimensional space and regressed onto a plane. So, if the dimensionality of the data is "n," the dimensionality of the space it is regressed on is "n - 1". The number of wavelengths used for the calibration is the number of dimensions.

The procedure for getting the best results includes understanding the regression process; knowing how to identify and deal with deviations from the "best straight line" such as outliers, nonlinearity of the regression line, failure of the regression model, error in the independent as well as the dependent variable and other extraneous sources of error; and knowing when and how to include chemical/spectroscopic information and interpret the regression statistics.

It is important, when discussing FTIR spectral interpretation by chemometrics, to differentiate between condensed phase and gas phase spectral interpretation. Compounds in the gas phase do not have the effects from changes in hydrogen bonding, the dielectric constant of the medium, and the nonpolar solvent-solute interactions⁽⁷⁾. Previous studies of automated spectral analysis of gas-phase FTIR spectral data have used various data reduction algorithms. The quantitative analysis of twelve hydrocarbons in a gaseous mixture were determined simultaneously by FTIR using the classical least squares (CLS) method⁽³²⁾. The precision of the results was 4% relative standard deviation and the concentrations were determined with an error of less than 10%.

A least squares fit (LSF) method, sometimes referred to as classical least squares (CLS), of data analysis was applied to six mixtures of vapors of industrial hygiene concern in ambient air. The concentration range of the two to six component mixtures was from 50 ppm to 100 ppb⁽⁵⁾. The LSF method was used to quantify strongly overlapping multicomponent mixtures. The results obtained support the conclusion that the FTIR spectrometer used with the LSF method is appropriate for the direct quantification of multicomponent mixtures of many airborne gases and vapors.

A commercially available LSF program was applied to trace organic vapors in impurity and moisture-free air⁽⁷⁾. In this study three mixtures were used. The mixtures contained five to eleven components each and the concentrations of the components were approximately 2 ppm. Equations for sensitivity and specificity are given as: sensitivity = true positives / (true positives + false negatives) and specificity = true negatives / (true negatives + false positives). It is mentioned that specificity can only be improved at the expense of sensitivity and vice versa.

It is likely that one or more data reduction algorithms may be found that will interpret the data collected onboard spacecraft and report results in a useful manner to NASA. The algorithm used for data analysis must be efficient, fast, and accurate. The algorithm should be rugged and able to adapt as the needs for monitoring and data reduction change.

5.0 Instrumentation and Hardware Considerations

In addition to data analysis requirements, NASA has unique data collection system requirements. The requirements for the data collection system must be examined, including: safety, size, power requirements, weight, ruggedness, interferometric scan speed, signal to noise ratio, and long-term stability. Although NASA may require instrumentation that is unique and not available commercially, it is logical to examine the commercially available hardware and examine it against NASA's needs.

Before examining the specific needs of NASA for hardware, a survey of commercially available systems and their components was completed. There are few commercially available OP-FTIR monitoring systems, when compared to the number of laboratory FTIR systems available. Open-path monitoring systems are different than laboratory spectrometers because they have telescoping optics to focus the energy from a source that is comparatively far from the detector (Figure 2). The systems are not usually sold with sampling cells, but rather with telescoping optics and tripods.

The monitoring systems surveyed had many of the same recommended components with slight variations and different options. The systems surveyed were all based on the continuous scan Michelson interferometer. Interferometer designs attempt to be durable and mechanically stable. The number of movable parts and the requirement for re-alignment is minimized in each design. One vendor recommended a porch swing Michelson interferometer⁽³⁹⁾ as was designed by Walker and Rex.

The vendors recommended that the beamsplitter and any required optics be made of ZnSe (Zinc Selenide) because it is not hygroscopic. The most commonly used material for laboratory systems is KBr which is less expensive, but hygroscopic. Under the controlled conditions of a laboratory, the components can be kept free from moisture. Since the moisture level encountered outside the laboratory varies greatly and instrumental repairs or configuration changes are done in the open air, ZnSe is recommended. Although this is an issue for general open-path spectrometry, this may not be an issue in the controlled spacecraft environment. However, it is important to consider the duration of the flight and whether ZnSe or some other material offers the best combination of qualities for a space mission.

The recommended detector is a mercury cadmium telluride (MCT) detector. The MCT detector is sensitive and offers quick response time for real-time monitoring. The MCT detector is cooled with liquid N₂. The standard dewar supplied with the detector will remain cool for approximately 12 hours. For long-term monitoring applications, such as this one, a Sterling cooler or a closed-cycle cryocooler may be used to cool the detector. Although the MCT detector is recommended for open-path monitoring, other detectors or the best way to keep the detector cool should be examined. MCT detectors are inherently non-linear and corrections to this non-linearity are often used. Close attention should be paid to the inherent non-linearity as well as methods of cooling the detector.

The highest spectral resolution of the systems examined varied between 0.5 cm^{-1} and 1 cm^{-1} . A resolution study should be performed during the experimental portion of this program to determine the optimum spectral resolution for the specific set of compounds for this application. There may be more than one spectral resolution that is appropriate for different subsets of the measured compounds. A qualitative detection scheme might consist of answering the questions in the following logical sequence:

- Were any of the compounds on the list observed above their SMAC limit?
- Which one(s)?
- What is the relative importance of the compound?

Importance of the compound triggers an action which might be to look at the data further. Further investigations of the data might be to:

- Check one or more confirmatory data peaks or confer with a complementary monitoring technique;
- Run a data analysis algorithm on the data which is more thorough than the routine data analysis package (which is more time efficient) and more compound specific but more time intensive;
- Trigger an action within the cabin, such as checking for a leak; or, in the case of an acutely dangerous compound, trigger an alternative analysis for confirmation.

A quantitative detection scheme might consist of answering questions in the following logical sequence:

- Were any of the compounds on the list observed above their SMAC limit?
- Which one(s)?
- What was the concentration observed?
- Over what time frame?
- How does this compare with the SMAC limit?
- What is the relative importance of this compound?
- What is the time scale of the observed event, was it a short term or a long-term observation?
- If it was a short term observation, and it was not much above the SMAC limit - is any action required for his observed compound?

- If it was a long-term observation is the concentration changing in time?
- How quickly is it changing in time?
- Is the concentration increasing or decreasing?
- If the concentration is increasing, how quickly?
- Is there an immediate risk to life for the concentration observed and the compound?

A trade-off analysis of data collection time, data storage requirements, data analysis time, data analysis computational intensity, and data analysis accuracy and precision should be done. The optimum spectral and time resolution should be determined for future work.

The greatest variance in monitoring systems was in the size and weight of the spectrometers and the associated hardware. The spectrometer size was from 9"x9"x14" (LxWxH) and 20 lb. to much larger depending on the components housed in the spectrometer compartment. Large telescope optics are included in the instruments and may not be necessary for NASA's application. Commercially available systems must be able to monitor in many different scenarios, but NASA has a very well defined monitoring scenario and instrumental components can be designed to meet the specific needs for monitoring on spacecraft. A trade off of the optimum optical configuration should be done to determine the best combination of the instrumental size, pathlength for monitoring the compounds of interest, geometry for assessing the cabin and best construction material for instrumental components.

Although the perfect monitoring system to meet NASA's needs is not likely to be commercially available, it is important to learn from the manufacturers of commercially available hardware. The monitoring system needs to make sense for the exact suite of compounds that are to be observed and some of the general requirements may ultimately be unimportant.

6.0 Potential of OP-FTIR Applicability to Spacecraft Monitoring

The foregoing analysis and discussion provides strong evidence of the feasibility of OP-FTIR for characterization of trace-level air contaminants in the environmental control systems for various space applications. There would appear to be several modes of application stemming from some unique characteristics and advantages of the using the open-path monitoring configuration of FTIR. Characteristics of the combined technique (FTIR plus Open-path) in the areas of data collection and data analysis are detailed.

A brief listing of some characteristics in the area of data collection is helpful:

- Multiple open paths permit collection of IR data throughout a volume region using IR beams guided by mirror and reflector optics as well as multiple sources and detectors;
- Multiple fan path or similar techniques for obtaining data via optical beam arrays can permit analysis of three-dimensional representations of air composition and location within the spacecraft volume via tomographic reconstruction techniques;
- Data collection may be continual at collection speeds of up to several spectra per second (with current hardware configurations);
- The free air flow of the open-path configuration (which can, of course, be assisted by air fans and blowers at appropriate locations) requires no active sampling with its consequential losses or skewing of trace components;
- OP-FTIR offers a “volumetric region” rather than a “point” sampling technique by definition;
- Data collection is not impacted by breakage of the IR beam since data on all frequencies are collected simultaneously, so data collection can be stopped when the beam is occluded (by a “floating body” for example) and resumed when the beam reappears with appropriate time tags noting the interruption; and
- The FTIR beam is low energy density (unlike a laser beam) and is thus inherently safe for use in areas of unprotected human eyes such as in a spacecraft cabin.

Likewise, a brief listing of characteristics in the area of data analysis includes:

- All collected data can be archived as interferometric data or can be subjected to initial Fourier transformation and stored as digitized “conventional “ spectra;

Data analysis can be done at any time, real-time or post collection;

- Data analysis strategies can be varied according to need -- for example, the analysis can look only at spectral peak frequencies to monitor for indication of peaks and then perform a more detailed spectral analysis of regions of interest without immediate need for additional data collection;
- Spectral features such as peak and band shape can be examined for confirmation of identity of suspected contaminant species; and
- Data can be co-added in a moving average mode to enable evaluation of the data for trends in time.

These characteristics suggest that the OP-FTIR monitoring technique could provide the baseline trace contaminant measurements for most of the SMAC list species. The ability to collect and analyze data at several levels of detail and to employ the power of co-addition to improve the signal-to-noise ratio for more sensitive detection, as well as for more reliable confirmation of identity, represents a unique capability worthy of further investigation.

In particular, the potential exploitation of tomographic approaches to revealing and understanding the formation and flow of trace contaminants in life support systems is key to the development and operation of advanced systems for support of planetary bases and long-term space exploration vehicles.

OP-FTIR can be used to obtain a characterization of the air in the spacecraft cabin. Multiple paths can be set up within the cabin to monitor the environment. One or more FTIR instruments may be used to collect the data for analysis on-board spacecraft or for transfer to Earth for interpretation. Data reduction algorithms may be used to determine the presence (or absence) of compounds that the algorithm has been trained to recognize. Data may be stored and referenced if there is some question of the presence of a compound from earlier in the mission or past missions.

7.0 Summary of Results and Conclusions

This project examines the applicability of OP-FTIR for monitoring spacecraft environments. The specific applicability of the OP-FTIR monitoring technique to the target list of compounds with SMAC exposure limits was shown using a spectral library that contained 111 of the 198 compounds with SMAC limits. The optimum peak for each compound was determined based on minimum overlap with atmospheric water and carbon dioxide, selecting pathlengths in the 1- to 50-meter range and having an observed detection at the SMAC level. The list of optimum peak absorbance ranges is shown in Table 1 (alphabetical) and Table 2 (listed by peak location).

Typical pathlengths that are required to monitor compounds at their SMAC exposure limit were determined for one-hour and 7-day exposure times. To determine the pathlength range, Beer's law was used with a minimum absorbance of 0.005 and a maximum absorbance of 0.8. Generally, two pathlengths for monitoring were recommended to assure that most compounds would be observed within the absorbance range that allows quantitation.

Detection of compounds at the one-hour SMAC exposure levels requires using a 15 centimeter and a 25-meter pathlength and all but five compounds are detected at or below their SMAC one-hour exposure concentration. If an additional pathlength of 100 meters is added, three of the five compounds may be observed; however, optical alignment and throughput may be difficulties at this pathlength. Large pathlengths for detection at the one-hour SMAC exposure for acrolein and methylhydrazine are required. The SMAC limits for these compounds for one hour are 0.013 ppm and 0.0021 ppm, respectively. The low limit of detection in this case results in the need for a high pathlength to monitor the compounds. The next highest path requirements is for hydrogen sulfide. The SMAC exposure limit for this compounds is 15 ppm, however, it is not a very good absorber of infrared energy. Therefore, the pathlength required for monitoring the compound must be greater than 96 meters.

Detection of compounds at the 7-day SMAC exposure levels requires using a 20 centimeter path and a 40-meter path and all but 7 of the SMAC compounds in the infrared library can be detected at or below their SMAC exposure limit. Of the seven remaining compounds: one of the seven would be detected at a 100-meter pathlength, two of the seven would be detected at a 270-meter pathlength, and three of the seven would be detected at a 420-meter pathlength. It might be reasonable to include a 100 - meter pathlength, but the importance of the compound (nitrogen dioxide), cost for additional equipment, cost for additional analysis, and impact on the measurement frequency along the other pathlengths should be considered in decisions such as this one. Of the compounds not observed with a 40-meter pathlength, the 7-day SMAC exposure limits vary from 0.0021 ppm for methylhydrazine to 2.0 ppm for hydrogen sulfide. So, again, it is a combination of detection limit and the inherent strength of infrared absorption that determine the overall pathlength required for analysis.

These characteristics suggest that the OP-FTIR monitoring technique could provide the baseline trace contaminant measurements for most of the SMAC list species. The ability to collect and analyze data at several levels of detail and to employ the power of co-addition to improve the signal-to-noise ratio for more sensitive detection, as well as for more reliable confirmation of identity, represents a unique capability worthy of investigation. In particular, the potential exploitation of tomographic approaches to revealing and understanding the formation and flow of trace contaminants in life support systems is key to the development and operation of advanced systems for support of planetary bases and long-term space exploration vehicles.

8.0 Recommendations for Future Direction

Future NASA efforts should follow this feasibility investigation of OP-FTIR spectrometry measurement technology. Areas that need further investigation include, but may not be limited to, demonstrating the applicability of OP-FTIR, comparing OP-FTIR to other technologies, modeling, chemometrics studies, and a resolution study.

The applicability of OP-FTIR technology should be demonstrated by conducting confirmatory experimental tests with commercially available hardware. These tests should include monitoring applications that mimic space travel and hardware modifications and revisions should be made as needed. The data from these multi-analyte tests should be used to perform preliminary evaluations of the available data reduction algorithms suitable for analysis. The data reduction algorithms, like the hardware, should be modified to best suit this particular application.

OP-FTIR should be compared to other available technologies for general applicability and /or as one detection method in a suite of detection methods. Comparison and complementary methodologies should include those which have been identified for measuring the same suite of trace contaminants. The compounds on the SMAC list should be prioritized so that monitoring and detection strategy can be focused on those compounds of most importance. The logical sequence of the detection scheme should be further developed to include more detail of the events that are to occur when a compound is observed at or above its SMAC limit. It may be appropriate for NASA to develop SMAC exposure levels for longer duration flights as the mission times increase. Many compounds only contain SMAC data for 7 days, the data set should be completed for these compounds.

Modeling and chemometrics studies should be done for the number and types of compounds anticipated during space travel. The modeling effort for point source monitoring should be complemented by effort using tomography for path-averaged data. Considerable investigations into the available hardware and the appropriate modifications for NASA's needs should be done. The commercially available equipment is made to be used for a wide variety of monitoring applications, NASA has very specific needs. Considerable creative thought should go into determining the type of detector to use that best suits NASA's needs.

A study of the appropriate spectral and time resolution for monitoring for this application should be conducted. This could be a laboratory test that incorporates the compounds anticipated during space travel. Laboratory assessments may be done in a calibration cell, but some tests should be performed in an environmental chamber. The simulated environment should best mimic the environment anticipated during travel.

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Figures

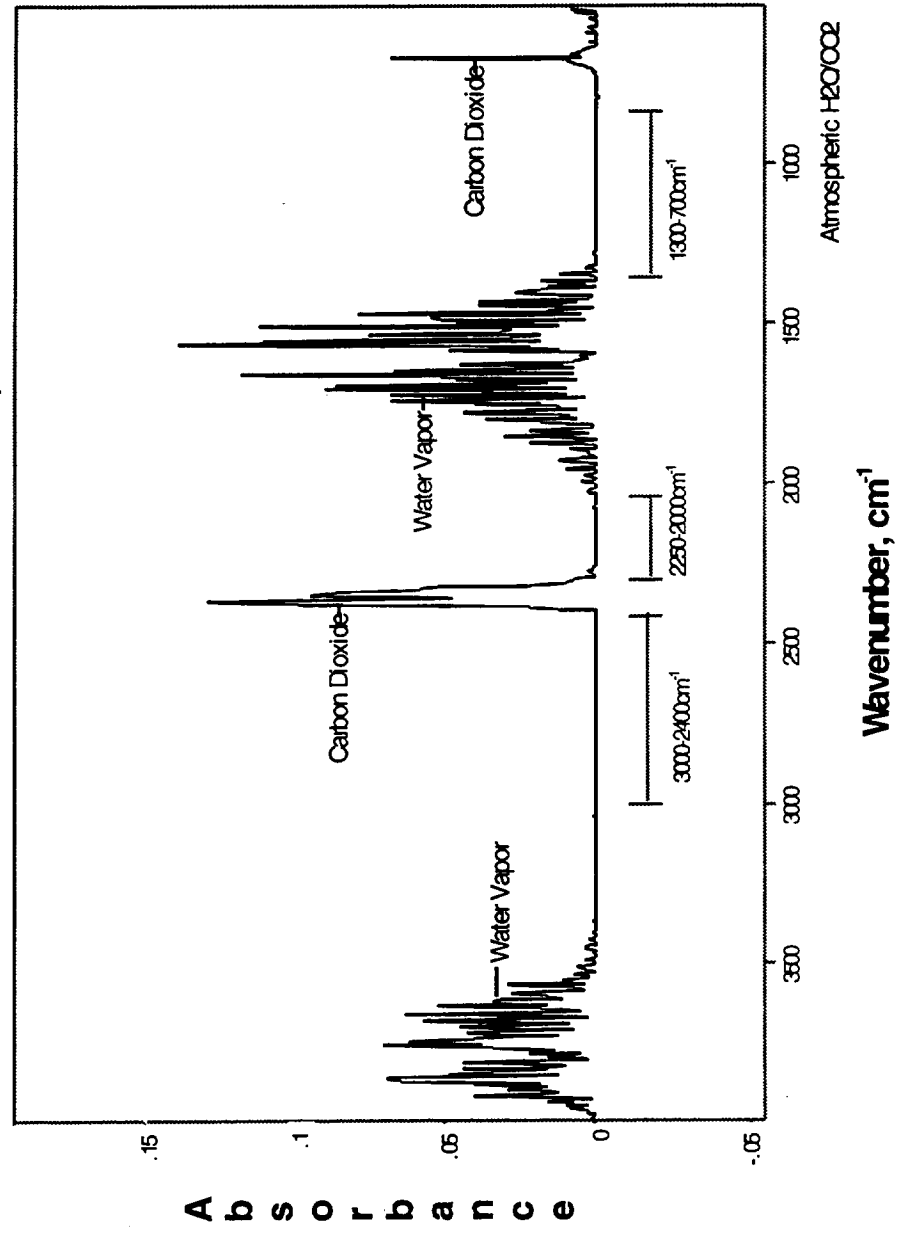


Figure 1: FTIR Spectrum of Atmospheric Carbon Dioxide and Water

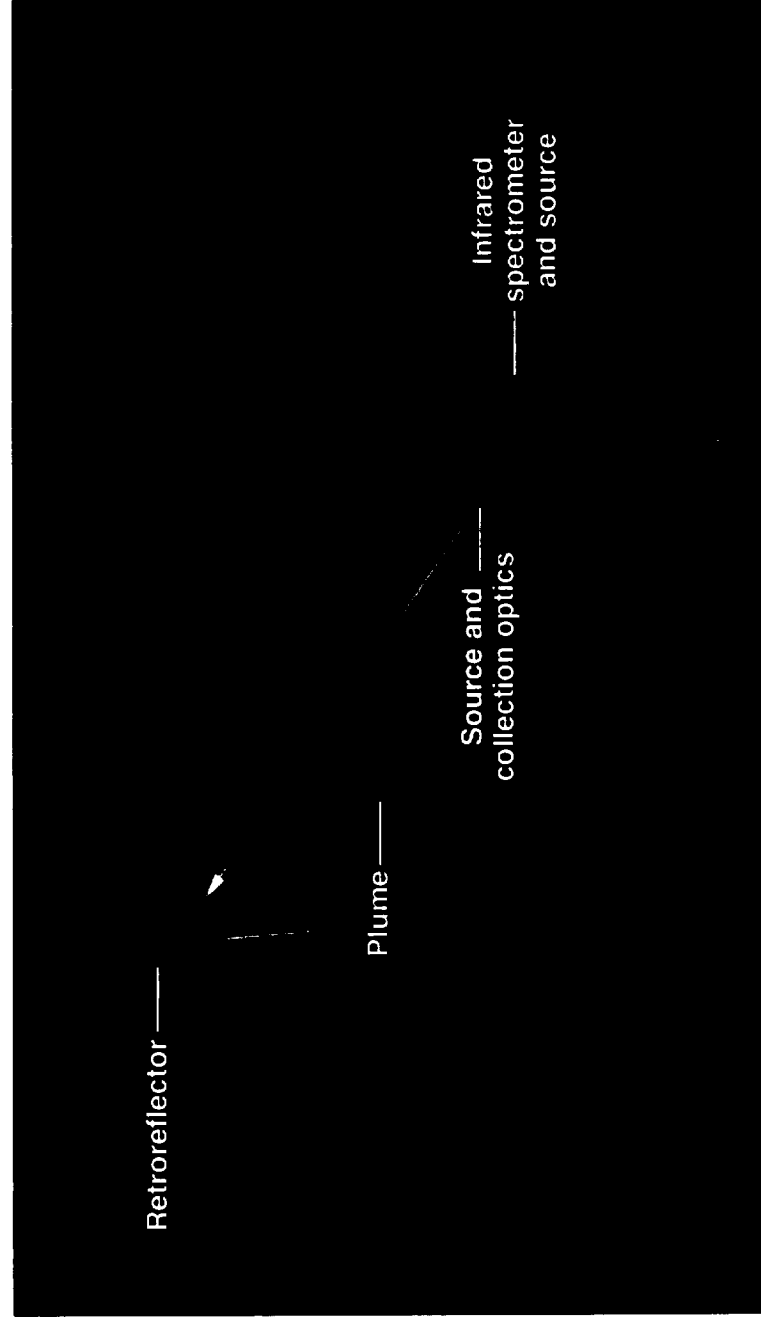


Figure 2. OP-FTIR Monitoring System

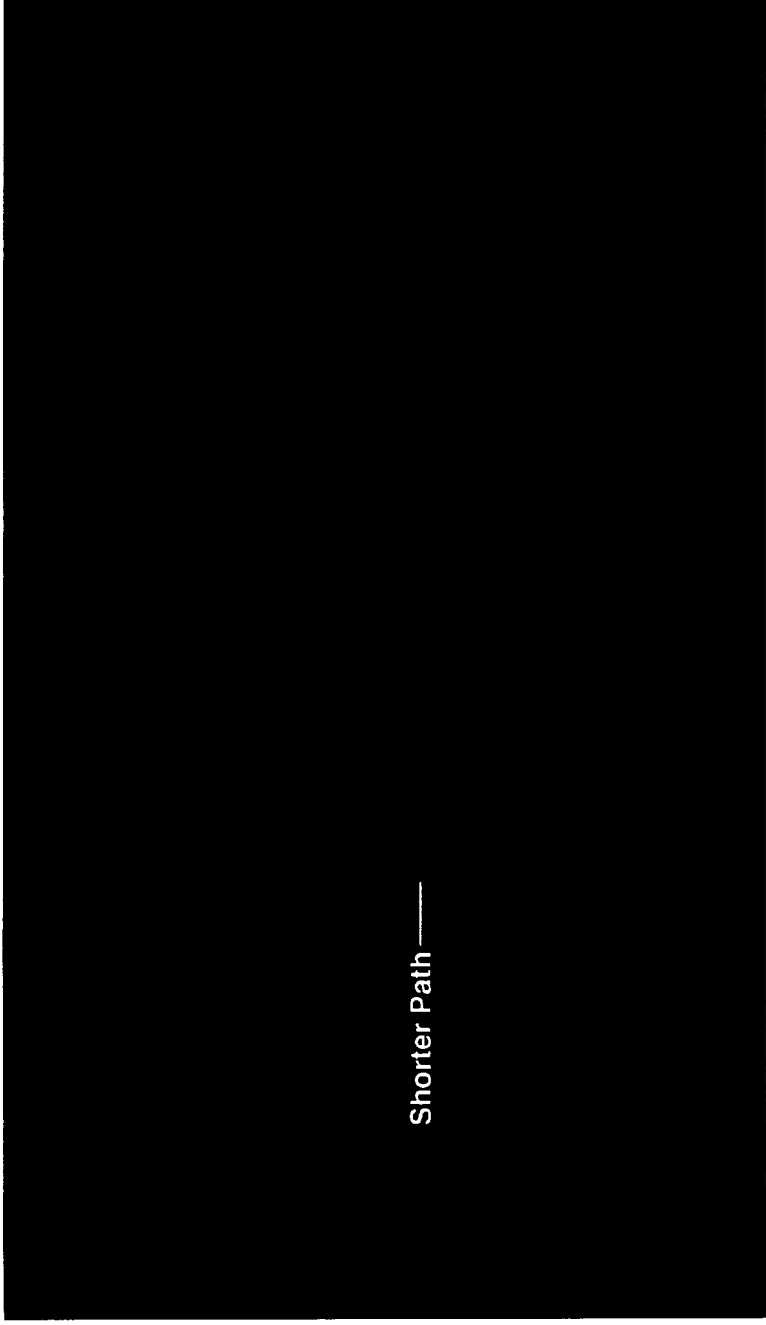


Figure 3a. Multiple Pathlength Optical Configuration

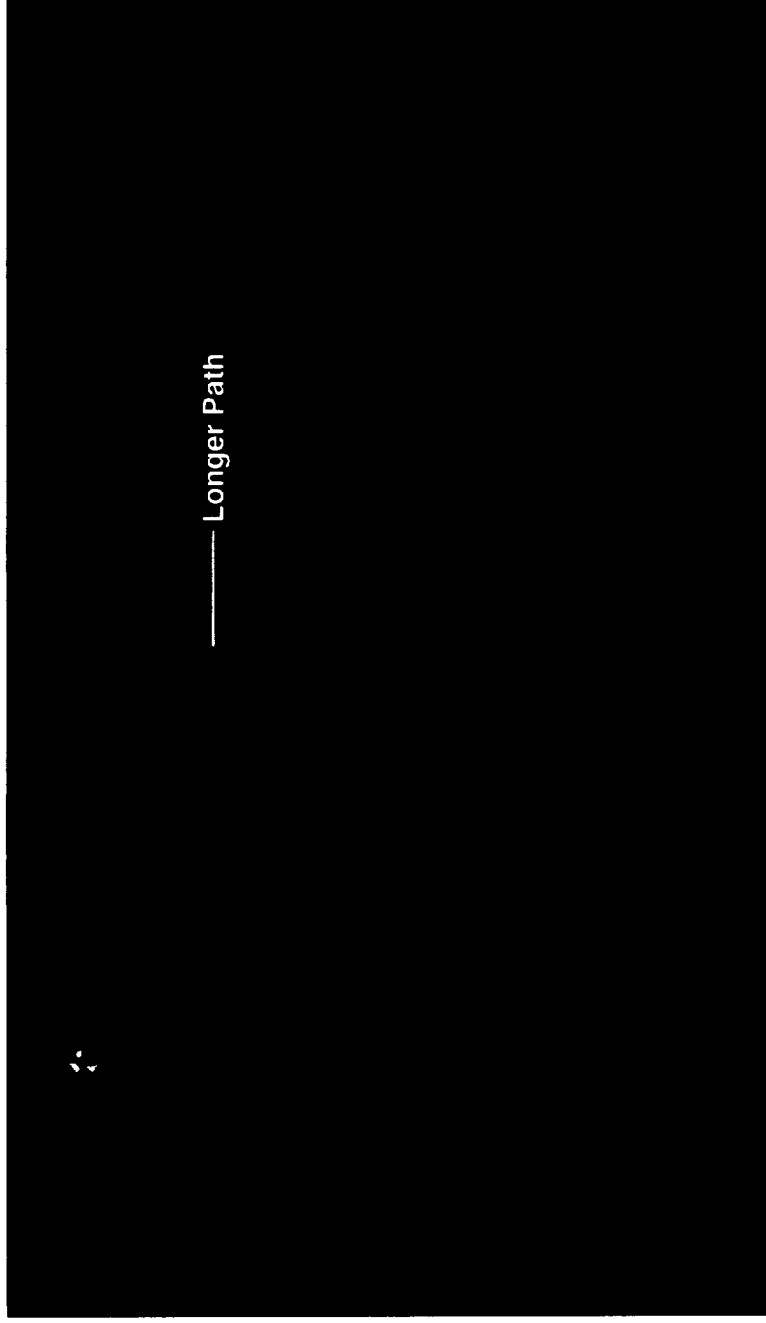


Figure 3b. Multiple Pathlength Optical Configuration

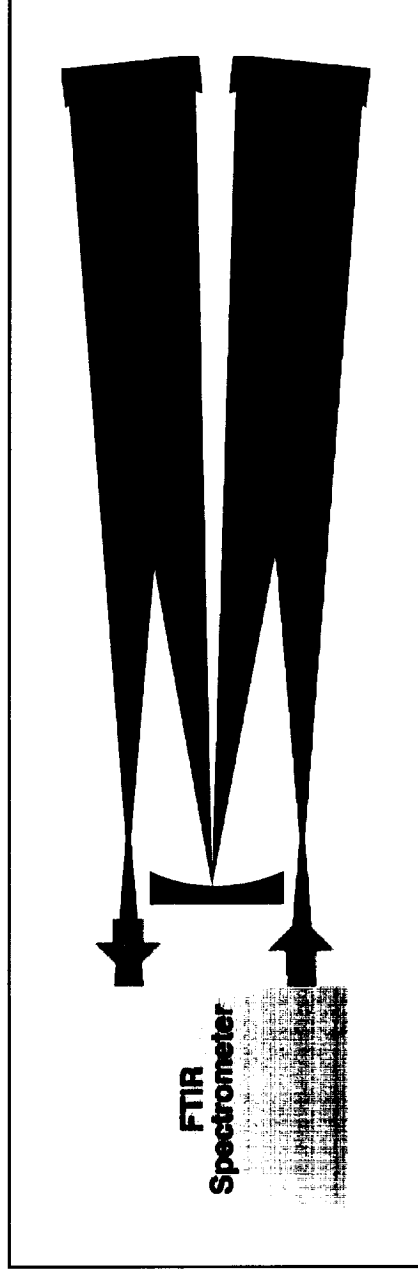


Figure 4. Multiple Pass Optical Configuration

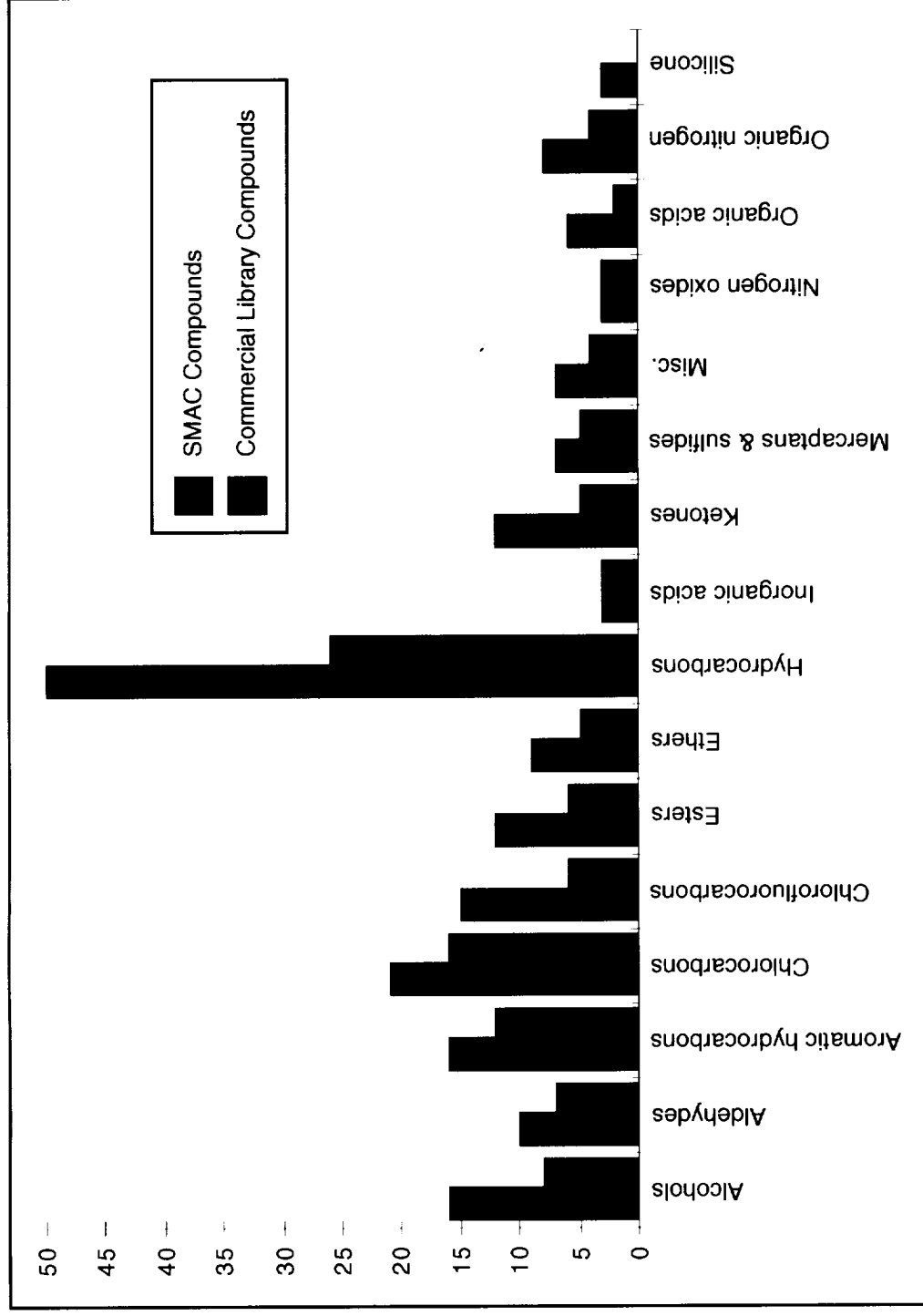


Figure 5. SMAC Compounds by Chemical Class in the Spectral Library

Tables

Table 1: Alphabetical Sort of Optimum Peaks for SMAC Compounds Peak Selected to Minimize Spectral Overlap With Atmospheric Water and Carbon Dioxide at Pathlengths Between 1 and 50 Meters for SMAC Levels.

Compound Name	Upper Frequency Bound (cm-1)	Lower Frequency Bound (cm-1)
Acetaldehyde	2897	2600
Acetic acid	1224	1126
Acetone	1138	1052
Acetonitrile	1096	981
Acetophenone	1283	1225
Acetylene	915	913
Acrolein	1037	884
Allyl alcohol	741	677
Ammonia	1212	730
Benzaldehyde	765	716
Benzene	703	639
Bromotrifluoromethane	781	743
Butane	3045	2809
1-Butanol	1139	981
1-Butene	1037	963
cis-2-Butene	2964	2815
trans-2-Butene	1018	901
n-Butyl acetate	2902	2836
Butyraldehyde	2850	2771
Carbon disulfide	2200	2160
Carbon monoxide	2228	2055
Carbon tetrachloride	815	786
Carbonyl sulfide	2088	2021
Chlorobenzene	769	652
Chloroethane	1013	942
Chloroform	806	729
Chloromethane	773	675
Crotonaldehyde	1176	1117
Cyclohexane	928	856
Cyclohexene	1300	1223
Cyclopentene	939	855
Cyclopropane	948	793
1,2-Dichlorobenzene	1056	1026
1,1-Dichloroethane	1310	1200
1,2-Dichloroethane	733	651
Dichloromethane	1291	1245
1,2-Dichloropropane	1046	988
Diethyl ether	951	793
Diisopropyl ether	2959	2916
Dimethyl sulfide	3036	2820
Dodecane	2879	2843
Ethane	909	761
Ethanol	920	845
Ethyl acetate	881	825
Ethyl formate	2956	2870
Ethylbenzene	927	868
Ethylene	925	920
Formaldehyde	3071	2627

Compound Name	Upper Frequency Bound (cm-1)	Lower Frequency Bound (cm-1)
Freon 11	960	908
Freon 113	1236	1002
Freon 114	751	721
Freon 12	1126	1048
Freon 22	1205	1058
Furan	789	706
Heptane	3004	2955
Hexane	3010	2837
Hydrazine	1026	864
Hydrogen chloride	3060	2652
Hydrogen cyanide	779	691
Hydrogen fluoride	4205	3693
Hydrogen sulfide	1455	912
Isobutane	1191	1150
Isobutyl alcohol	3011	2824
Isobutylene	1313	1250
Isoprene	1096	1050
Isopropylbenzene	1296	1254
Mesitylene	859	815
Methane	3189	2868
Methanol	1081	971
Methyl acetate	870	800
2-Methylbutane	3019	2834
Methyl butyl ketone	3003	2840
Methyl ethyl ketone	1237	1054
Methyl isobutyl ketone	1257	1224
Methyl mercapton	2989	2905
Methyl methacrylate	1047	970
3-Methylpentane	3005	2949
Methyl vinyl ether	1040	926
Methylhydrazine	933	838
Naphthalene	809	732
Nitric oxide	1951	1800
Nitrogen dioxide	2937	2858
Nitromethane	694	618
Nitrous oxide	1330	1219
Octane	2898	2832
Pentane	766	703
1-Pentene	3044	2812
2-Pentene	3090	2806
Phenol	1215	1162
Propane	753	745
1-Propanol	1133	1064
2-Propanol	849	786
Propanoic acid	1367	1213
Propionaldehyde	2871	2767
n-Propyl acetate	990	950
Propylbenzene	2994	2957
Propylene	1047	1044
Styrene	733	650
Sulfur dioxide	2526	2459
Tetrachloroethane	868	798
Tetrahydrofuran	980	844

Compound Name	Upper Frequency Bound (cm-1)	Lower Frequency Bound (cm-1)
Toluene	758	669
1,1,1-Trichloroethane	1076	1057
1,1,2-Trichloroethane	2992	2958
1,2,4-Trimethylbenzene	1290	1257
Trichloroethylene	862	828
Vinyl chloride	990	916
Vinylidene chloride	902	842
m-Xylene	802	737
o-Xylene	1057	1052
p-Xylene	831	715

Table 2: Peak Beginning Sort of Optimum Peaks for SMAC Compounds. Peaks Were Selected to Minimize Spectral Overlap With Atmospheric Water and Carbon Dioxide at Pathlengths Between 1 and 50 Meters for SMAC Levels.

Compound Name	Upper Frequency Bound (cm ⁻¹)	Lower Frequency Bound (cm ⁻¹)
Nitromethane	694	618
Benzene	703	639
1,2-Dichloroethane	733	651
Styrene	733	650
Allyl alcohol	741	677
Freon 114	751	721
Propane	753	745
Toluene	758	669
Benzaldehyde	765	716
Pentane	766	703
Chlorobenzene	769	652
Chloromethane	773	675
Hydrogen cyanide	779	691
Bromotrifluoromethane	781	743
Furan	789	706
m-Xylene	802	737
Chloroform	806	729
Naphthalene	809	732
Carbon tetrachloride	815	786
p-Xylene	831	715
2-Propanol	849	786
Mesitylene	859	815
Trichloroethylene	862	828
Tetrachloroethane	868	798
Methyl acetate	870	800
Ethyl acetate	881	825
Vinylidene chloride	902	842
Ethane	909	761
Acetylene	915	913
Ethanol	920	845
Ethylene	925	920
Ethylbenzene	927	868
Cyclohexane	928	856
Methylhydrazine	933	838
Cyclopentene	939	855
Cyclopropane	948	793
Diethyl ether	951	793
Freon 11	960	908
Tetrahydrofuran	980	844
n-Propyl acetate	990	950
Vinyl chloride	990	916

Compound Name	Upper Frequency Bound (cm ⁻¹)	Lower Frequency Bound (cm ⁻¹)
Chloroethane	1013	942
trans-2-Butene	1018	901
Hydrazine	1026	864
1-Butene	1037	963
Acrolein	1037	884
Methyl vinyl ether	1040	926
1,2-Dichloropropane	1046	988
Methyl methacrylate	1047	970
Propylene	1047	1044
1,2-Dichlorobenzene	1056	1026
o-Xylene	1057	1052
1,1,1-Trichloroethane	1076	1057
Methanol	1081	971
Acetonitrile	1096	981
Isoprene	1096	1050
Freon 12	1126	1048
1-Propanol	1133	1064
Acetone	1138	1052
1-Butanol	1139	981
Crotonaldehyde	1176	1117
Isobutane	1191	1150
Freon 22	1205	1058
Ammonia	1212	730
Phenol	1215	1162
Acetic acid	1224	1126
Freon 113	1236	1002
Methyl ethyl ketone	1237	1054
Methyl isobutyl ketone	1257	1224
Acetophenone	1283	1225
1,2,4-Trimethylbenzene	1290	1257
Dichloromethane	1291	1245
Isopropylbenzene	1296	1254
Cyclohexene	1300	1223
1,1-Dichloroethane	1310	1200
Isobutylene	1313	1250
Nitrous oxide	1330	1219
Propanoic acid	1367	1213
Hydrogen sulfide	1455	912
Nitric oxide	1951	1800
Carbonyl sulfide	2088	2021
Carbon disulfide	2200	2160
Carbon monoxide	2228	2055
Sulfur dioxide	2526	2459
Butyraldehyde	2850	2771
Propionaldehyde	2871	2767

Compound Name	Upper Frequency Bound (cm ⁻¹)	Lower Frequency Bound (cm ⁻¹)
Dodecane	2879	2843
Acetaldehyde	2897	2600
Octane	2898	2832
n-Butyl acetate	2902	2836
Nitrogen dioxide	2937	2858
Ethyl formate	2956	2870
Diisopropyl ether	2959	2916
cis-2-Butene	2964	2815
Methyl mercapton	2989	2905
1,1,2-Trichloroethane	2992	2958
Propylbenzene	2994	2957
Methyl butyl ketone	3003	2840
Heptane	3004	2955
3-Methylpentane	3005	2949
Hexane	3010	2837
Isobutyl alcohol	3011	2824
2-Methylbutane	3019	2834
Dimethyl sulfide	3036	2820
1-Pentene	3044	2812
Butane	3045	2809
Hydrogen chloride	3060	2652
Formaldehyde	3071	2627
2-Pentene	3090	2806
Methane	3189	2868
Hydrogen fluoride	4205	3693

Table 3: Alphabetical Sort of One-hour SMAC Exposures in Pathlength Range for the Most Appropriate Peak for Each Compound (peaks in Table 1) with an On-scale Absorbance Between 0.005 Absorbance Units and 0.8 absorbance units for the One-hour SMAC Limits.

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Acetaldehyde	3.0	490
Acetic acid	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Acetone	0.48	77
Acetonitrile	4.8	780
Acetophenone	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Acetylene	0.14	22
Acrolein	210	33,000
Allyl alcohol	1.1	180
Ammonia	0.10	16
Benzaldehyde	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Benzene	0.082	13
Bromotrifluoromethane	0.0027	0.43
Butane	0.066	11
1-Butanol	0.34	55
1-Butene	0.41	66
cis-2-Butene	0.27	43
trans-2-Butene	0.28	44
n-Butyl acetate	0.18	29
Butyraldehyde	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Carbon disulfide	4.7	760
Carbon monoxide	0.19	31
Carbon tetrachloride	0.10	15
Carbonyl sulfide	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Chlorobenzene	0.75	120
Chloroethane	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Chloroform	0.088	14
Chloromethane	0.26	42
Crotonaldehyde	6.5	1040
Cyclohexane	0.12	20
Cyclohexene	0.93	150
Cyclopentene	0.66	110
Cyclopropane	0.40	63
1,2-Dichlorobenzene	0.37	59
1,1-Dichloroethane	0.51	82
1,2-Dichloroethane	20	3200
Dichloromethane	0.19	30
1,2-Dichloropropane	0.37	60
Diethyl ether	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Diisopropyl ether	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Dimethyl sulfide	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Dodecane	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Ethane	0.085	14
Ethanol	0.045	7.2
Ethyl acetate	0.13	21
Ethyl formate	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Ethylbenzene	0.94	151
Ethylene	0.059	9.4
Formaldehyde	27	4300
Freon 11	0.039	6.2
Freon 113	0.12	19
Freon 114	0.056	9.0
Freon 12	0.0011	0.17
Freon 22	0.00093	0.15
Furan	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Heptane	0.011	1.8
Hexane	0.10	16
Hydrazine	5.6	890
Hydrogen chloride	1.5	240
Hydrogen cyanide	15	2,500
Hydrogen fluoride	0.83	132
Hydrogen sulfide	96	15,000
Isobutane	0.026	4.1
Isobutyl alcohol	0.073	12
Isobutylene	0.14	22
Isoprene	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Isopropylbenzene	0.62	99
Mesitylene	0.22	35
Methane	0.0013	0.20
Methanol	0.23	36
Methyl acetate	0.21	34
2-Methylbutane	0.037	5.9
Methyl butyl ketone	1.0	170
Methyl ethyl ketone	0.34	54
Methyl isobutyl ketone	0.17	27
Methyl mercapton	84	13,000
Methyl methacrylate	0.39	63
3-Methylpentane	0.0082	1.3
Methyl vinyl ether	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Methylhydrazine	13,000	2,100,000
Naphthalene	1.4	224
Nitric oxide	0.34	55
Nitrogen dioxide	8.4	1,400
Nitromethane	2.0	320
Nitrous oxide	0.010	1.6

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Octane	0.025	4.1
Pentane	0.033	5.2
1-Pentene	0.17	26
2-Pentene	0.16	26
Phenol	0.84	140
Propane	0.38	61
1-Propanol	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
2-Propanol	0.62	99
Propanoic acid	0.89	140
Propionaldehyde	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
n-Propyl acetate	0.15	23
Propylbenzene	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Propylene	0.31	50
Styrene	0.079	13
Sulfur dioxide	5.6	890
Tetrachloroethane	0.079	13
Tetrahydrofuran	0.15	25
Toluene	0.44	71
1,1,1-Trichloroethane	0.042	6.8
1,1,2-Trichloroethane	1.4	220
Trichloroethylene	0.11	18
1,2,4-Trimethylbenzene	0.70	110
Vinyl chloride	0.077	12
Vinylidene chloride	0.98	160
m-Xylene	0.078	13
o-Xylene	1.4	220
p-Xylene	0.081	13

Table 4: Minimum Pathlength Sort of Compounds with One-hour SMAC Exposures in ppm
Pathlength Range for the Most Appropriate Peak for Each Compound (peaks in Table 1) With an On-
scale Absorbance Between 0.005 Absorbance Units (minimum path) and 0.8 Absorbance Units
(maximum path) for the One-hour SMAC Limits.

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Freon 22	0.00093	0.15
Freon 12	0.0011	0.17
Methane	0.0013	0.20
Bromotrifluoromethane	0.0027	0.43
3-Methylpentane	0.0082	1.3
Nitrous oxide	0.010	1.6
Heptane	0.011	1.8
Octane	0.025	4.1
Isobutane	0.026	4.1
Pentane	0.033	5.2
2-Methylbutane	0.037	5.9
Freon 11	0.039	6.2
1,1,1-Trichloroethane	0.042	6.8
Ethanol	0.045	7.2
Freon 114	0.056	9.0
Ethylene	0.059	9.4
Butane	0.066	11
Isobutyl alcohol	0.073	12
Vinyl chloride	0.077	12
m-Xylene	0.078	13
Styrene	0.079	13
Tetrachloroethane	0.079	13
p-Xylene	0.081	13
Benzene	0.082	13
Ethane	0.085	14
Chloroform	0.088	14
Carbon tetrachloride	0.10	15
Ammonia	0.10	16
Hexane	0.10	16
Trichloroethylene	0.11	18
Freon 113	0.12	19
Cyclohexane	0.12	20
Ethyl acetate	0.13	21
Isobutylene	0.14	22
Acetylene	0.14	22
n-Propyl acetate	0.15	23
Tetrahydrofuran	0.15	25
2-Pentene	0.16	26
1-Pentene	0.17	26
Methyl isobutyl ketone	0.17	27

Compound Name	Minimum Path (meters)	Maximum Path (meters)
n-Butyl acetate	0.18	29
Dichloromethane	0.19	30
Carbon monoxide	0.19	31
Methyl acetate	0.21	34
Mesitylene	0.22	35
Methanol	0.23	36
Chloromethane	0.26	42
cis-2-Butene	0.27	43
trans-2-Butene	0.28	44
Propylene	0.31	50
Methyl ethyl ketone	0.34	54
Nitric oxide	0.34	55
1-Butanol	0.34	55
o-Dichlorobenzene	0.37	59
1,2-Dichloropropane	0.37	60
Propane	0.38	61
Methyl methacrylate	0.39	63
Cyclopropane	0.40	63
1-Butene	0.41	66
Toluene	0.44	71
Acetone	0.48	77
1,1-Dichloroethane	0.51	82
2-Propanol	0.62	99
Isopropylbenzene	0.62	99
Cyclopentene	0.66	110
1,2,4-Trimethylbenzene	0.70	110
Chlorobenzene	0.75	120
Hydrogen fluoride	0.83	130
Phenol	0.84	140
Propanoic acid	0.89	140
Cyclohexene	0.93	150
Ethylbenzene	0.94	150
Vinylidene chloride	0.98	160
Methyl butyl ketone	1.0	170
Allyl alcohol	1.1	180
1,1,2-Trichloroethane	1.4	220
o-Xylene	1.4	220
Naphthalene	1.4	220
Hydrogen chloride	1.5	240
Nitromethane	2.0	320
Acetaldehyde	3.0	490
Carbon disulfide	4.7	760
Acetonitrile	4.8	780
Hydrazine	5.6	890
Sulfur dioxide	5.6	890

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Crontonaldehyde	6.5	1,000
Nitrogen dioxide	8.4	1,400
Hydrogen cyanide	15	2,500
1,2-Dichloroethane	20	3,200
Formaldehyde	27	4,300
Methyl mercapton	84	13,000
Hydrogen sulfide	96	15,000
Acrolein	209	33,000
Methylhydrazine	13132	2,100,000
1-Propanol	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Acetic acid	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Acetophenone	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Benzaldehyde	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Butyraldehyde	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Carbonyl sulfide	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Chloroethane	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Diethyl ether	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Diisopropyl ether	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Dimethyl sulfide	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Dodecane	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Ethyl formate	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Furan	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Isoprene	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Methyl vinyl ether	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Propionaldehyde	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit
Propylbenzene	No 1 Hour SMAC Limit	No 1 Hour SMAC Limit

Table 5: Alphabetical Sort of Compounds With 7-day SMAC Exposures in ppm Pathlength Range for the Most Appropriate Peak for Each Compound (peaks in Table 1) With an On-scale Absorbance Between 0.005 Absorbance Units (minimum path) and 0.8 Absorbance Units (maximum path) for the 7-day SMAC Limits.

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Acetaldehyde	15	2,400
Acetic acid	2.1	340
Acetone	12	1,900
Acetonitrile	36	5,800
Acetophenone	0.72	120
Acetylene	0.14	22
Acrolein	1,400	220,000
Allyl alcohol	23	3,600
Ammonia	0.28	45
Benzaldehyde	0.92	150
Benzene	1.9	310
Bromotrifluoromethane	0.0052	0.83
Butane	0.066	11
1-Butanol	0.0065	1.0
1-Butene	0.0041	0.66
trans-2-Butene	0.28	44
n-Butyl acetate	0.0091	1.5
Butyraldehyde	0.52	84
Carbon disulfide	8.9	1,400
Carbon monoxide	1.1	180
Carbon tetrachloride	0.44	71
Carbonyl sulfide	0.25	40
Chlorobenzene	0.75	120
Chloroethane	0.48	77
Chloroform	1.8	290
Chloromethane	1.3	210
cis-2-Butene	0.27	43
Crontonaldehyde	13	2,000
Cyclohexane	1.2	200
Cyclohexene	9.4	1,500
Cyclopentene	13	2,100
Cyclopropane	0.40	63
o-Dichlorobenzene	8.2	1,300
1,1-Dichloroethane	5.2	830
1,2-Dichloroethane	20	3,200
Dichloromethane	1.3	210
1,2-Dichloropropane	0.045	7.2
Diethyl ether	2.2	340
Diisopropyl ether	0.27	42
Dimethyl sulfide	18	3,000

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Dodecane	0.11	17
Ethane	0.085	14
Ethanol	0.090	14
Ethyl acetate	2.1	330
Ethyl formate	0.54	86
Ethylbenzene	5.8	930
Ethylene	0.059	9.4
Formaldehyde	270	43,000
Freon 11	0.39	62
Freon 113	0.12	19
Freon 114	1.1	180
Freon 12	0.022	3.5
Freon 22	0.019	3.0
Furan	29	4,700
Heptane	0.11	18
Hexane	0.10	16
Hydrazine	560	89,000
Hydrogen chloride	8.0	1,300
Hydrogen cyanide	15	2,500
Hydrogen fluoride	17	2,600
Hydrogen sulfide	720	110,000
Isobutane	0.026	4.1
Isobutyl alcohol	0.18	29
Isobutylene	0.14	22
Isoprene	0.66	110
Isopropylbenzene	4.1	660
Mesitylene	3.7	580
Methane	0.0013	0.20
Methanol	1.0	160
Methyl acetate	1.4	220
2-Methylbutane	0.037	5.9
Methyl butyl ketone	2.1	330
Methyl ethyl ketone	1.7	270
Methyl isobutyl ketone	0.0017	0.27
Methyl mercapton	420	67,000
Methyl methacrylate	3.2	520
3-Methylpentane	0.0082	1.3
Methyl vinyl ether	0.33	53
Methylhydrazine	13,000	2,100,000
Naphthalene	2.1	330
Nitric oxide	2.0	310
Nitrogen dioxide	81	13,000
Nitromethane	7.1	1,100
Nitrous oxide	0.0015	0.23
Octane	0.13	21

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Pentane	0.033	5.2
1-Pentene	0.17	26
2-Pentene	0.16	26
Phenol	4.2	670
Propane	0.38	61
Propanoic acid	3.5	570
1-Propanol	0.34	54
2-Propanol	4.1	660
Propionaldehyde	0.79	130
n-Propyl acetate	0.90	140
Propylbenzene	0.84	140
Propylene	0.31	50
Styrene	0.78	120
Sulfur dioxide	21	3,400
Tetrachloroethane	3.2	510
Tetrahydrofuran	0.95	150
Toluene	0.44	71
1,1,1-Trichloroethane	0.65	100
1,1,2-Trichloroethane	0.049	7.9
Trichloroethylene	0.61	98
1,2,4-Trimethylbenzene	0.12	19
Vinyl chloride	8.5	1,400
Vinylidene chloride	2.5	400
m-Xylene	0.15	24
o-Xylene	2.7	430
p-Xylene	0.16	25

Table 6: Minimum Pathlength Sort of Compounds With 7-day SMAC Exposures in ppm Pathlength Range for the Most Appropriate Peak for Each Compound (peaks in Table 1) With an On-Scale Absorbance Between 0.005 Absorbance Units (minimum path) and 0.8 Absorbance Units (maximum path) for the 7-day SMAC Limits.

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Methane	0.0013	0.20
Nitrous oxide	0.0015	0.23
Methyl isobutyl ketone	0.0017	0.27
1-Butene	0.0041	0.66
Bromotrifluoromethane	0.0052	0.83
1-Butanol	0.0065	1.0
3-Methylpentane	0.0082	1.3
n-Butyl acetate	0.0091	1.5
Freon 22	0.019	3.0
Freon 12	0.022	3.5
Isobutane	0.026	4.1
Pentane	0.033	5.2
2-Methylbutane	0.037	5.9
1,2-Dichloropropane	0.045	7.2
1,1,2-Trichloroethane	0.049	7.9
Ethylene	0.059	9.4
Butane	0.066	11
Ethane	0.085	14
Ethanol	0.090	14
Hexane	0.10	16
Dodecane	0.11	17
Heptane	0.11	18
1,2,4-Trimethylbenzene	0.12	19
Freon 113	0.12	19
Octane	0.13	21
Isobutylene	0.14	22
Acetylene	0.14	22
m-Xylene	0.15	24
p-Xylene	0.16	25
2-Pentene	0.16	26
1-Pentene	0.17	26
Isobutyl alcohol	0.18	29
Carbonyl sulfide	0.25	40
Diisopropyl ether	0.27	42
cis-2-Butene	0.27	43
trans-2-Butene	0.28	44
Ammonia	0.28	45
Propylene	0.31	50
Methyl vinyl ether	0.33	53
1-Propanol	0.34	54

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Propane	0.38	61
Freon11	0.39	62
Cyclopropane	0.40	63
Toluene	0.44	71
Carbon tetrachloride	0.44	71
Chloroethane	0.48	77
Butyraldehyde	0.52	84
Ethyl formate	0.54	86
Trichloroethylene	0.61	98
1,1,1-Trichloroethane	0.65	100
Isoprene	0.66	110
Acetophenone	0.72	120
Chlorobenzene	0.75	120
Styrene	0.78	120
Propionaldehyde	0.79	130
Propylbenzene	0.84	140
n-Propyl acetate	0.90	140
Benzaldehyde	0.92	150
Tetrahydrofuran	0.95	150
Methanol	1.0	160
Freon 114	1.1	180
Carbon monoxide	1.1	180
Cyclohexane	1.2	200
Dichloromethane	1.3	210
Chloromethane	1.3	210
Methyl acetate	1.4	220
Methyl ethyl ketone	1.7	270
Chloroform	1.8	290
Benzene	1.9	310
Nitric oxide	2.0	310
Ethyl acetate	2.1	330
Methyl butyl ketone	2.1	330
Naphthalene	2.1	330
Acetic acid	2.1	340
Diethyl ether	2.2	340
Vinylidene chloride	2.5	400
o-Xylene	2.7	430
Tetrachloroethane	3.2	510
Methyl methacrylate	3.2	520
Propanoic acid	3.5	570
Mesitylene	3.7	580
Isopropylbenzene	4.1	660
2-Propanol	4.1	660
Phenol	4.2	670
1,1-Dichloroethane	5.2	830

Compound Name	Minimum Path (meters)	Maximum Path (meters)
Ethylbenzene	5.8	930
Nitromethane	7.1	1,100
Hydrogen chloride	8.0	1,300
o-Dichlorobenzene	8.2	1,300
Vinyl chloride	8.5	1,400
Carbon disulfide	8.9	1,400
Cyclohexene	9.4	1,500
Acetone	12	1,900
Crotonaldehyde	13	2,000
Cyclopentene	13	2,100
Acetaldehyde	15	2,400
Hydrogen cyanide	15	2,500
Hydrogen fluoride	17	2,600
Dimethyl sulfide	18	3,000
1,2-Dichloroethane	20	3,200
Sulfur dioxide	21	3,400
Allyl alcohol	23	3,600
Furan	29	4,700
Acetonitrile	36	5,800
Nitrogen dioxide	81	13,000
Formaldehyde	270	43,000
Methyl mercaptan	420	67,000
Hydrazine	560	89,000
Hydrogen sulfide	720	110,000
Acrolein	1,400	220,000
Methylhydrazine	13,000	2,100,000

Appendix A

List of SMAC Compounds in the Spectral Library and Their Respective Exposure Limits for Seven Exposure Times.

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hours	7 days	30 days	180 days	365 days	600 days
Acetaldehyde	11	5.5	2.2	2.2	2.2	2.2	2.2
Acetic acid	NA	NA	3.0	0.68	0.11	0.056	0.036
Acetone	500	210	21	21	21	21	21
Acetonitrile	29	20	3.9	NA	NA	NA	NA
Acetophenone	NA	NA	10	10	10	10	10
Acetylene	490	490	490	490	490	490	490
Acrolein	0.087	0.035	0.013	0.013	0.013	0.013	0.013
Allyl alcohol	8.3	4.1	0.41	0.41	0.41	0.41	0.41
Ammonia	28	20	10	10	10	10	10
Benzaldehyde	NA	NA	39	39	39	39	39
Benzene	11	3.1	0.46	0.092	0.062	0.031	0.018
Bromotrifluoromethane	3400	3400	1800	1800	1800	1800	1800
Butane	99	99	99	99	99	99	99
1-Butanol	49	26	26	26	26	26	26
1-Butene	200	200	200	200	200	200	200
cis-2-Butene	99	99	99	99	99	99	99
trans-2-Butene	100	100	100	99	99	99	99
n-Butyl acetate	200	150	39	39	39	39	39
Butyraldehyde	NA	NA	40	40	40	40	40
Carbon disulfide	9.5	9.5	5.1	NA	NA	NA	NA
Carbon monoxide	52	17	8.6	8.6	8.6	8.6	8.6
Carbon tetrachloride	9.4	4.7	2.0	0.47	0.078	0.039	0.023
Carbonyl sulfide	NA	NA	4.8	NA	NA	NA	NA
Chlorobenzene	10	10	10	10	10	10	10
Chloroethane	NA	NA	97	NA	NA	NA	NA
Chloroform	20	10	1.0	NA	NA	NA	NA
Chloromethane	100	50	20	4.8	0.95	0.48	0.081
Crotonaldehyde	4.1	2.1	2.1	2.1	2.1	2.1	2.1
Cyclohexane	600	300	60	60	60	60	60
Cyclohexene	590	300	59	59	59	59	59
Cyclopentene	60	60	60	60	60	60	60
Cyclopropane	57	57	57	57	57	57	57
1,2-Dichlorobenzene	110	74	4.9	4.9	4.9	4.9	4.9
1,1-Dichloroethane	240	200	24	24	24	24	24
1,2-Dichloroethane	0.49	0.49	0.49	0.49	0.24	0.12	0.075
Dichloromethane	99	34	14	5.7	2.8	1.4	0.71
1,2-Dichloropropane	110	75	8.9	8.9	8.9	8.9	8.9
Diethyl ether	NA	NA	78	NA	NA	NA	NA
Diisopropyl ether	NA	NA	49	NA	NA	NA	NA
Dimethyl sulfide	NA	NA	0.97	0.97	0.97	0.97	0.97
Dodecane	NA	NA	40	NA	NA	NA	NA
Ethane	960	960	960	960	960	960	960
Ethanol	2100	2100	1000	1000	1000	1000	1000

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hours	7 days	30 days	180 days	365 days	600 days
Ethyl acetate	770	380	49	49	49	49	49
Ethyl formate	NA	NA	30	NA	NA	NA	NA
Ethylbenzene	180	57	29	29	29	29	29
Ethylene	290	290	290	290	290	290	290
Formaldehyde	0.40	0.10	0.040	0.040	0.040	0.040	0.040
Freon11	980	980	98	98	98	98	98
Freon113	51	51	51	51	51	51	51
Freon114	2000	980	98	98	98	98	98
Freon12	2000	980	97	97	97	97	97
Freon22	1900	970	97	97	97	97	97
Furan	NA	NA	0.039	NA	NA	NA	NA
Heptane	480	380	48	NA	NA	NA	NA
Hexane	50	50	50	50	50	50	50
Hydrazine	3.8	0.3	0.038	0.023	0.0038	NA	NA
Hydrogen chloride	5.3	2.0	0.99	0.99	0.99	0.99	0.99
Hydrogen cyanide	0.62	0.62	0.62	0.62	0.62	0.62	0.62
Hydrogen fluoride	2.4	1.2	0.12	0.12	0.12	0.12	0.12
Hydrogen sulfide	15	10	2.0	NA	NA	NA	NA
Isobutane	99	99	99	99	99	99	99
Isobutyl alcohol	97	49	39	39	39	39	39
Isobutylene	470	470	470	470	470	470	470
Isoprene	NA	NA	200	200	200	200	200
Isopropylbenzene	98	49	15	15	15	15	15
Mesitylene	50	25	3.0	3.0	3.0	3.0	3.0
Methane	5700	5700	5700	5700	5700	5700	5700
Methanol	30	10	6.8	6.8	6.8	6.8	6.8
Methyl acetate	250	200	39	39	39	39	39
2-Methylbutane	100	100	100	100	100	100	100
Methyl butyl ketone	10	5.0	5.0	5.0	5.0	5.0	5.0
Methyl ethyl ketone	50	50	10	10	10	10	10
Methyl isobutyl ketone	34	34	34	34	34	34	34
Methyl mercapton	0.5	0.25	0.10	NA	NA	NA	NA
Methyl methacrylate	200	99	24	24	24	24	24
Methyl vinyl ether	NA	NA	50	NA	NA	NA	NA
Methylhydrazine	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021
3-Methylpentane	500	500	500	500	500	500	500
Naphthalene	2.8	1.9	1.9	1.9	1.9	1.9	1.9
Nitric Oxide	28	24	4.9	NA	NA	NA	NA
Nitrogen Dioxide	4.7	2.6	0.49	NA	NA	NA	NA
Nitromethane	26	16	7.1	7.1	5.1	NA	NA
Nitrous Oxide	49	25	490	NA	NA	NA	NA
Octane	380	300	74	NA	NA	NA	NA
Pentane	200	200	200	200	200	200	200
1-Pentene	65	65	65	65	65	65	65

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hours	7 days	30 days	180 days	365 days	600 days
2-Pentene	65	65	65	65	65	65	65
Phenol	10	5	2	NA	NA	NA	NA
Propane	490	490	490	490	490	490	490
Propanoic Acid	19	10	4.9	4.9	4.9	4.9	4.9
1-Propanol	NA	NA	39	39	39	39	39
2-Propanol	400	96	60	60	60	60	60
Propionaldehyde	NA	NA	39	39	39	39	39
n-Propyl acetate	250	200	40	40	40	40	40
Propylbenzene	NA	NA	10	NA	NA	NA	NA
Propylene	490	490	490	490	490	490	490
Styrene	100	50	10	10	10	10	10
Sulfur dioxide	3.8	1.9	0.98	0.98	0.98	0.98	0.98
Tetrachloroethane	200	49	4.9	1.2	0.20	0.10	0.058
Tetrahydrofuran	250	200	40	NA	NA	NA	NA
1,1,1-Trichloroethane	440	340	29	29	29	29	29
1,1,2-Trichloroethane	3.6	1.8	0.99	NA	NA	NA	NA
1,2,4-Trimethylbenzene	50	25	3.0	3.0	3.0	3.0	3.0
Toluene	16	16	16	16	16	16	16
Trichloroethylene	49	11	9.2	3.7	1.8	0.92	0.46
Vinyl chloride	130	29	1.2	1.2	1.2	1.2	1.2
Vinylidene chloride	5.0	2.5	2.0	0.50	0.082	0.037	0.022
m-Xylene	97	97	50	50	50	50	50
o-Xylene	100	100	50	50	50	50	50
p-Xylene	97	97	50	50	50	50	50

Appendix B

Complete List of SMAC Compounds and Exposure Limits for Seven Exposure Times.

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Acetaldehyde	11	5.5	2.2	2.2	2.2	2.2	2.2
Acetic acid	NA	NA	3.0	0.68	0.11	0.056	0.036
Acetone	500	210	21	21	21	21	21
Acetonitrile	29	20	3.9	NA	NA	NA	NA
Acetophenone	NA	NA	10	10	10	10	10
Acetylene	490	490	490	490	490	490	490
Acrolein	0.087	0.035	0.013	0.013	0.013	0.013	0.013
Allene	NA	NA	49	NA	NA	NA	NA
Allyl alcohol	8.3	4.1	0.41	0.41	0.41	0.41	0.41
Ammonia	28	20	10	10	10	10	10
n-Amyl acetate	190	97	30	30	30	30	30
Benzaldehyde	NA	NA	39	39	39	39	39
Benzene	11	3.1	0.46	0.092	0.062	0.031	0.018
1-Benzo(e)pyrole	1.0	0.31	0.051	0.051	0.051	0.051	0.051
Bromotrifluoromethane	3400	3400	1800	1800	1800	1800	1800
1,2-Butadiene	1.8	1.8	0.31	0.13	0.058	0.029	0.018
Butane	99	99	99	99	99	99	99
1-Butanol	49	26	26	26	26	26	26
2-Butanol	200	99	39	39	39	39	39
1-Butene	200	200	200	200	200	200	200
cis-2-Butene	99	99	99	99	99	99	99
trans-2-Butene	99	99	99	99	99	99	99
n-Butyl acetate	200	150	39	39	39	39	39
tert-Butyl alcohol	150	97	39	39	39	39	39
Butyl chloride	NA	NA	39	39	39	39	39
1-Butyne	80	80	80	80	80	80	80
Butyraldehyde	NA	NA	40	40	40	40	40
Butyric acid	NA	NA	4.9	4.9	4.9	4.9	4.9
Caprylic acid	NA	NA	25	25	25	25	25
Carbon dioxide	13000	13000	7100	7100	7100	7100	7100
Carbon disulfide	9.5	9.5	5.1	NA	NA	NA	NA
Carbon monoxide	52	17	8.6	8.6	8.6	8.6	8.6
Carbon tetrachloride	9.4	4.7	2.0	0.47	0.078	0.039	0.023
Carbonyl sulfide	NA	NA	4.8	NA	NA	NA	NA
Chlorine	1	0.5	0.30	0.30	0.30	0.30	0.30
Chloroacetone	1	0.49	0.049	0.049	0.049	0.049	0.049
Chlorobenzene	10	10	10	10	10	10	10
Chloroethane	NA	NA	97	NA	NA	NA	NA
Chlorofluoromethane	NA	NA	49	12	1.9	0.97	0.6
Chloroform	20	10	1.0	NA	NA	NA	NA
Chloromethane	100	50	20	4.8	0.95	0.48	0.081
Chlorotrifluoroethane	NA	NA	97	NA	NA	NA	NA

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Chlorotrifluoroethene	NA	NA	99	NA	NA	NA	NA
Crontonaldehyde	4.1	2.1	2.1	2.1	2.1	2.1	2.1
Cyanamide	NA	NA	0.8	NA	NA	NA	NA
Cyclohexane	600	300	60	60	60	60	60
Cyclohexanol	96	48	29	29	29	29	29
Cyclohexanone	49	25	15	15	15	15	15
Cyclohexene	590	300	59	59	59	59	59
Cyclopentane	1200	590	58	58	58	58	58
Cyclopentene	60	60	60	60	60	60	60
Cyclopropane	57	57	57	57	57	57	57
Decalin	NA	NA	1.9	1.9	1.9	1.9	1.9
Decane	39	39	39	39	39	39	39
Dichloracetylene	0.61	0.041	0.03	0.025	0.015	0.008	0.0038
1,2-Dichlorobenzene	110	74	4.9	4.9	4.9	4.9	4.9
1,2-Dichloro-1,2-difluoroethene	NA	NA	25	NA	NA	NA	NA
1,1-Dichloroethane	240	200	24	24	24	24	24
1,2-Dichloroethane	0.49	0.49	0.49	0.49	0.24	0.12	0.075
Dichloromethane	99	34	14	5.7	2.8	1.4	0.71
1,2-Dichloropropane	110	75	8.9	8.9	8.9	8.9	8.9
Diethyl ether	NA	NA	78	NA	NA	NA	NA
Diethyl sulfide	NA	NA	0.97	NA	NA	NA	NA
Diisobutylketone	49	25	10	10	10	10	10
Diisopropyl ether	NA	NA	49	NA	NA	NA	NA
2,2-Dimethylbutane	25	25	25	25	25	25	25
1,1-Dimethylcyclohexane	26	26	26	26	26	26	26
trans-1,2-Dimethylcyclohexane	26	26	26	26	26	26	26
2,5-Dimethylfuran	NA	NA	0.04	NA	NA	NA	NA
1,2-Dimethyl hydrazine	NA	NA	0.1	0.024	0.004	0.002	0.0012
Dimethyl sulfide	NA	NA	0.97	0.97	0.97	0.97	0.97
1,3-Dioxane	49	25	4.9	1.2	0.20	0.10	0.063
Dodecane	NA	NA	40	NA	NA	NA	NA
Ethane	960	960	960	960	960	960	960
Ethanethiol	0.19	0.39	0.097	NA	NA	NA	NA
Ethanol	2100	2100	1000	1000	1000	1000	1000
2-Ethoxyethanol	11	11	0.8	0.53	0.08	0.04	0.024
2-Ethoxyethyl acetate	10	4.9	29	29	29	29	29
Ethyl acetate	770	380	49	49	49	49	49
Ethyl butyl ether	NA	NA	78	78	78	78	78
Ethyl formate	NA	NA	30	NA	NA	NA	NA
Ethyl lactate	NA	NA	52	NA	NA	NA	NA
1-Ethyl-2-methylbenzene	NA	NA	35	NA	NA	NA	NA
Ethylbenzene	180	57	29	29	29	29	29
Ethylene	290	290	290	290	290	290	290

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Ethylene glycol	23	23	5.0	5.0	5.0	5.0	5.0
Formaldehyde	0.40	0.10	0.040	0.040	0.040	0.040	0.040
Freon 11	980	980	98	98	98	98	98
Freon 112	990	500	98	98	98	98	98
Freon 113	51	51	51	51	51	51	51
Freon 114	2000	980	98	98	98	98	98
Freon 12	2000	990	97	97	97	97	97
Freon 21	19	9.0	5.0	5.0	5.0	5.0	5.0
Freon 22	1900	1000	97	97	97	97	97
Freon 23	NA	NA	100	NA	NA	NA	NA
Furan	NA	NA	0.039	NA	NA	NA	NA
Furfural	4.0	2.0	2.0	2.0	2.0	2.0	2.0
Gluteraldehyde	0.12	0.019	0.006	0.0029	0.00048	0.00024	0.00014
Halon 1301	3400	1800	1800	1800	1800	1800	1800
Heptane	480	380	48	NA	NA	NA	NA
1-Heptene	49	49	49	49	49	49	49
Hexamethylcyclotrisiloxane	NA	NA	25	NA	NA	NA	NA
Hexane	50	50	50	50	50	50	50
2-Hexanol	NA	NA	40	40	40	40	40
1-Hexene	51	51	51	51	51	51	51
Hydrazine	3.8	0.3	0.038	0.023	0.0038	NA	NA
Hydrogen	4000	4000	4000	4000	4000	4000	4000
Hydrogen chloride	5.3	2.0	0.99	0.99	0.00	0.99	0.99
Hydrogen cyanide	0.62	0.62	0.62	0.62	0.62	0.62	0.62
Hydrogen fluoride	2.4	1.2	0.12	0.12	0.12	0.12	0.12
Hydrogen sulfide	15	10	2.0	NA	NA	NA	NA
Indonaphthene	20	10	2.0	2.0	2.0	2.0	2.0
Isobutane	99	99	99	99	99	99	99
Isobutyl acetate	290	150	39	39	39	39	39
Isobutyl alcohol	97	49	39	39	39	39	39
Isobutylene	470	470	470	470	470	470	470
Isoprene	NA	NA	200	200	200	200	200
Isopropyl acetate	180	150	49	NA	NA	NA	NA
Isopropyl chloride	NA	NA	83	NA	NA	NA	NA
Isopropylbenzene	98	49	15	15	15	15	15
Limonene	NA	NA	99	NA	NA	NA	NA
Mercury	0.012	0.0024	0.0012	0.0012	0.0012	0.0012	0.0012
Mesitylene	50	25	3.0	3.0	3.0	3.0	3.0
Methane	5700	5700	5700	5700	5700	5700	5700
Methanol	30	10	6.8	6.8	6.8	6.8	6.8
Methyl acetate	250	200	39	39	39	39	39
2-Methylbutane	100	100	100	100	100	100	100
2-Methyl-1-butene	480	480	480	480	480	480	480
Methyl butyl ketone	10	5.0	5.0	5.0	5.0	5.0	5.0

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Methyl butyrate	NA	NA	20	NA	NA	NA	NA
trans-1-Methyl-3-ethylcyclohexane	NA	NA	25	NA	NA	NA	NA
Methyl ethyl ketone	50	50	10	10	10	10	10
Methyl hexyl ketone	NA	NA	19	NA	NA	NA	NA
3-Methyl indole	NA	NA	0.1	NA	NA	NA	NA
Methyl isobutyl ketone	34	34	34	34	34	34	34
Methyl mercapton	0.5	0.25	0.1	NA	NA	NA	NA
Methyl methacrylate	200	99	24	24	24	24	24
Methyl propyl ketone	20	20	20	20	20	20	20
Methyl styrene	99	49	28	28	28	28	28
Methyl vinyl ether	NA	NA	50	NA	NA	NA	NA
Methylcyclohexane	NA	NA	15	NA	NA	NA	NA
4-Methylcyclohexene	NA	NA	98	NA	NA	NA	NA
Methylcyclopentane	15	15	15	15	15	15	15
2-Methylfuran	NA	NA	0.038	NA	NA	NA	NA
Methylhydrazine	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021
3-Methylpentane	500	500	500	500	500	500	500
4-Methyl-3-penten-2-one	25	15	10	NA	NA	NA	NA
Monochlorofluoroethylene	NA	NA	25	NA	NA	NA	NA
Naphthalene	2.8	1.9	1.9	1.9	1.9	1.9	1.9
Nitric Oxide	28	24	4.9	NA	NA	NA	NA
Nitrogen Dioxide	4.7	2.6	0.49	NA	NA	NA	NA
Nitromethane	26	16	7.1	7.1	5.1	NA	NA
Nitrous Oxide	49	25	490	NA	NA	NA	NA
Nonane	60	60	60	60	60	60	60
1-Nonene	NA	NA	50	NA	NA	NA	NA
Octamethyltrisiloxane	410	200	100	20	4.1	NA	NA
Octane	380	300	74	NA	NA	NA	NA
1-Octanol	NA	NA	39	39	39	39	39
1-Octene	NA	NA	49	NA	NA	NA	NA
Pentane	200	200	200	200	200	200	200
1-Pentanol	NA	NA	35	35	35	35	35
1-Pentene	65	65	65	65	65	65	65
2-Pentene	65	65	65	65	65	65	65
Phenol	10	4.9	2.0	NA	NA	NA	NA
Phorone	NA	NA	19	NA	NA	NA	NA
Propane	490	490	490	490	490	490	490
Propanoic acid	19	10	4.9	4.9	4.9	4.9	4.9
1-Propanol	NA	NA	39	39	39	39	39
2-Propanol	400	96	60	60	60	60	60
Propionaldehyde	NA	NA	39	39	39	39	39
n-Propyl acetate	250	200	40	40	40	40	40
n-Propyl chloride	NA	NA	29	29	29	29	29

	SMAC Limits for Trace Gas Contaminants, in ppm, for Specified Durations						
Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Propylbenzene	NA	NA	10	NA	NA	NA	NA
Propylene	490	490	490	490	490	490	490
Propyne	250	250	250	250	250	250	250
Pyruvic acid	NA	NA	1.0	NA	NA	NA	NA
Styrene	98	50	10	10	10	10	10
Sulfur dioxide	3.8	1.9	0.98	0.98	0.98	0.98	0.98
Tetrachloroethane	200	49	4.9	1.2	0.2	0.1	0.058
Tetradecane	50	50	50	50	50	50	50
Tetrafluoroethene	NA	NA	48	48	48	48	48
Tetrahydrofuran	250	200	40	NA	NA	NA	NA
1,1,1-Trichloroethane	440	340	29	29	29	29	29
1,1,2-Trichloroethane	3.6	1.8	0.99	NA	NA	NA	NA
1,2,4-Trimethylbenzene	50	25	3.0	3.0	3.0	3.0	3.0
1,1,3-Trimethylcyclohexane	NA	NA	24	NA	NA	NA	NA
2,2,4-Trimethylcyclohexane	NA	NA	68	NA	NA	NA	NA
Toluene	16	16	16	16	16	16	16
Trichloroethylene	49	11	9.2	3.7	1.8	0.92	0.46
Trimethylsilanol	160	19	11	11	11	11	11
Undecane	NA	NA	49	NA	NA	NA	NA
Valeraldehyde	96	48	30	30	30	30	30
Valeric acid	NA	NA	24	NA	NA	NA	NA
Vinyl chloride	130	29	1.2	1.2	1.2	1.2	1.2
Vinylidene chloride	5.0	2.5	2.0	0.50	0.082	0.037	0.022
m-Xylene	97	97	50	50	50	50	50
o-Xylene	97	97	50	50	50	50	50
p-Xylene	97	97	50	50	50	50	50

Appendix B

Complete List of SMAC Compounds and Exposure Limits for Seven Exposure Times.

Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Acetaldehyde	11	5.5	2.2	2.2	2.2	2.2	2.2
Acetic acid	NA	NA	3.0	0.68	0.11	0.056	0.036
Acetone	500	210	21	21	21	21	21
Acetonitrile	29	20	3.9	NA	NA	NA	NA
Acetophenone	NA	NA	10	10	10	10	10
Acetylene	490	490	490	490	490	490	490
Acrolein	0.087	0.035	0.013	0.013	0.013	0.013	0.013
Allene	NA	NA	49	NA	NA	NA	NA
Allyl alcohol	8.3	4.1	0.41	0.41	0.41	0.41	0.41
Ammonia	28	20	10	10	10	10	10
Amyl Acetate	194	97	30	30	30	30	30
Benzaldehyde	NA	NA	39	39	39	39	39
Benzene	11	3.1	0.46	0.092	0.062	0.031	0.018
Benzo(e)pyrole	1.03	0.31	0.051	0.051	0.051	0.051	0.051
Bromotrifluoromethane	3400	3400	1800	1800	1800	1800	1800
Butadiene	1.8	1.8	0.31	0.13	0.058	0.029	0.018
Butyl acetate	200	150	39	39	39	39	39
Butane	99	99	99	99	99	99	99
Butanol	49	26	26	26	26	26	26
Butanol	195	99	39	39	39	39	39
Butene	197	197	197	197	197	197	197
Butyl Chloride	NA	NA	39	39	39	39	39
Butyne	80	80	80	80	80	80	80
Butyraldehyde	NA	NA	40	40	40	40	40
Butyric acid	NA	NA	4.9	4.9	4.9	4.9	4.9
Caprylic acid	NA	NA	25	25	25	25	25
Carbon dioxide	13000	13000	7100	7100	7100	7100	7100
Carbon disulfide	9.5	9.5	5.1	NA	NA	NA	NA
Carbon Monoxide	52	17	8.6	8.6	8.6	8.6	8.6
Carbon tetrachloride	9.4	4.7	2.0	0.47	0.078	0.039	0.023
Carbonyl sulfide	NA	NA	5	NA	NA	NA	NA
Chlorine	1	0.5	0.30	0.30	0.30	0.30	0.30
Chloroacetone	1	0.49	0.049	0.049	0.049	0.049	0.049
Chlorobenzene	10	10	10	10	10	10	10
Chloroethane	NA	NA	97	NA	NA	NA	NA
Chlorofluoromethane	NA	NA	49	12	1.9	0.97	0.6
Chloroform	20	10	1.0	NA	NA	NA	NA
Chloromethane	100	50	20	4.8	0.95	0.48	0.081
Chlorotrifluoroethane	NA	NA	97	NA	NA	NA	NA
Chlorotrifluoroethene	NA	NA	99	NA	NA	NA	NA
Butene	99	99	99	99	99	99	99
Crtonaldehyde	4.1	2.1	2.1	2.1	2.1	2.1	2.1
Cyanamide	NA	NA	0.8	NA	NA	NA	NA
Cyclohexane	600	300	60	60	60	60	60
Cyclohexanol	96	48	29	29	29	29	29
Cyclohexanone	49	25	15	15	15	15	15

Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Cyclohexene	590	300	59	59	59	59	59
Cyclopentane	1200	590	58	58	58	58	58
Cyclopentene	60	60	60	60	60	60	60
Cyclopropane	57	57	57	57	57	57	57
Decalin	NA	NA	1.9	1.9	1.9	1.9	1.9
Dioxane	49	25	4.9	1.2	0.20	0.10	0.063
Decane	39	39	39	39	39	39	39
Dichlorobenzene	NA	NA	4.9	4.9	4.9	4.9	4.9
Dichloroacetylene	0.61	0.041	0.03	0.025	0.015	0.008	0.0038
Dichloro-Difluoroethene	NA	NA	25	NA	NA	NA	NA
Dichloroethane	240	200	24	24	24	24	24
Dichloroethane	0.49	0.49	0.49	0.49	0.24	0.12	0.075
Dichloromethane	99	34	14	5.7	2.8	1.4	0.71
Dichloropropane	110	75	8.9	8.9	8.9	8.9	8.9
Diethyl ether	NA	NA	78	NA	NA	NA	NA
Diethyl sulfide	NA	NA	0.97	NA	NA	NA	NA
Diisobutylketone	49	25	10	10	10	10	10
Diisopropyl ether	NA	NA	49	NA	NA	NA	NA
Dimethylcyclohexane	26	26	26	26	26	26	26
Dimethyl hydrazine	NA	NA	0.1	0.024	0.004	0.002	0.0012
Dimethylbutane	25	25	25	25	25	25	25
Dimethylfuran	NA	NA	0.04	NA	NA	NA	NA
Dimethyl sulfide	NA	NA	0.97	0.97	0.97	0.97	0.97
Dodecane	NA	NA	40	NA	NA	NA	NA
Ethane	960	960	960	960	960	960	960
Ethanethiol	0.19	0.39	0.097	NA	NA	NA	NA
Ethanol	2100	2100	1000	1000	1000	1000	1000
Ethoxyethanol	11	11	0.8	0.53	0.08	0.04	0.024
Ethoxyethyl acetate	10	4.9	29	29	29	29	29
Ethyl acetate	770	380	49	49	49	49	49
Ethyl butyl ether	NA	NA	78	78	78	78	78
Ethyl formate	NA	NA	30	NA	NA	NA	NA
Ethyl lactate	NA	NA	52	NA	NA	NA	NA
Ethylbenzene	181	57	29	29	29	29	29
Ethylene	290	290	290	290	290	290	290
Ethyl-methylbenzene	NA	NA	35	NA	NA	NA	NA
Ethylene glycol	23	23	5.0	5.0	5.0	5.0	5.0
Formaldehyde	0.40	0.10	0.040	0.040	0.040	0.040	0.040
Freon 11	980	980	98	98	98	98	98
Freon 112	990	500	98	98	98	98	98
Freon 113	51	51	51	51	51	51	51
Freon 114	2000	980	98	98	98	98	98
Freon 12	2000	990	97	97	97	97	97
Freon 21	19	9.0	5.0	5.0	5.0	5.0	5.0
Freon 22	1900	1000	97	97	97	97	97
Freon 23	NA	NA	100	NA	NA	NA	NA
Furan	NA	NA	0	NA	NA	NA	NA
Furfural	4.0	2.0	2.0	2.0	2.0	2.0	2.0

Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Gluteraldehyde	0.12	0.019	0.006	0.0029	0.00048	0.00024	0.00014
Halon 1301	3400	1800	1800	1800	1800	1800	1800
Heptane	480	384	48	NA	NA	NA	NA
Heptene	49	49	49	49	49	49	49
Hexamethylcyclotrisiloxane	NA	NA	25	NA	NA	NA	NA
Hexane	50	50	50	50	50	50	50
Hexanol	NA	NA	40	40	40	40	40
Hexene	51	51	51	51	51	51	51
Hydrazine	3.8	0.3	0.038	0.23	0.0038	NA	NA
Hydrogen	4000	4000	4000	4000	4000	4000	4000
Hydrogen chloride	5.3	2.0	0.99	0.99	0.00	0.99	0.99
Hydrogen cyanide	0.62	0.62	0.62	0.62	0.62	0.62	0.62
Hydrogen fluoride	2.4	1.2	0.12	0.12	0.12	0.12	0.12
Hydrogen sulfide	15	10	2.0	NA	NA	NA	NA
Indonaphthene	20	10	2.0	2.0	2.0	2.0	2.0
Isobutane	99	99	99	99	99	99	99
Isobutyl acetate	290	150	39	39	39	39	39
Isobutyl alcohol	97	49	39	39	39	39	39
Isobutylene	470	470	470	470	470	470	470
Isoprene	NA	NA	198	198	198	198	198
Isopropyl acetate	177	145	49	NA	NA	NA	NA
Isopropyl chloride	NA	NA	83	NA	NA	NA	NA
Isopropylbenzene	98	49	15	15	15	15	15
Limonene	NA	NA	99	NA	NA	NA	NA
Mercury	0.012	0.0024	0.0012	0.0012	0.0012	0.0012	0.0012
Mesitylene	50	25	3.0	3.0	3.0	3.0	3.0
Methane	5700	5700	5700	5700	5700	5700	5700
Methanol	30	10	6.8	6.8	6.8	6.8	6.8
Methyl acetate	250	200	39	39	39	39	39
Methylbutane	100	100	100	100	100	100	100
Methyl-1-butene	480	480	480	480	480	480	480
Methyl butyl ktone	10	5.0	5.0	5.0	5.0	5.0	5.0
Methyl butyrate	NA	NA	20	NA	NA	NA	NA
Methylcyclohexene	NA	NA	98	NA	NA	NA	NA
Methyl ethyl ketone	50	50	10	10	10	10	10
Methylfuran	NA	NA	0.038	NA	NA	NA	NA
Methyl hexyl ketone	NA	NA	19	NA	NA	NA	NA
Methyl indole	NA	NA	0.1	NA	NA	NA	NA
Methyl isobutyl ketone	34	34	34	34	34	34	34
Methyl mercapton	0.5	0.25	0.1	NA	NA	NA	NA
Methyl methacrylate	200	99	24	24	24	24	24
Methylpentane	500	500	500	500	500	500	500
Methyl-penten-one	25	15	10	NA	NA	NA	NA
Methyl propyl ketone	20	20	20	20	20	20	20
Methyl styrene	99	49	28	28	28	28	28
Methyl vinyl ether	NA	NA	50	NA	NA	NA	NA
Methylcyclohexane	NA	NA	15	NA	NA	NA	NA
Methylcyclopentane	15	15	15	15	15	15	15

Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Methylhydrazine	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021
Monochlorofluoroethylene	NA	NA	25	NA	NA	NA	NA
Naphthalene	2.8	1.9	1.9	1.9	1.9	1.9	1.9
Nitric Oxide	28	24	4.9	NA	NA	NA	NA
Nitrogen Dioxide	4.7	2.6	0.49	NA	NA	NA	NA
Nitromethane	26	16	7.1	7.1	5.1	NA	NA
Nitrous Oxide	49	25	490	NA	NA	NA	NA
Nonane	60	60	60	60	60	60	60
Nonene	NA	NA	50	NA	NA	NA	NA
Octamethyltrisiloxane	410	200	100	20	4.1	NA	NA
Octane	380	300	74	NA	NA	NA	NA
Octanol	NA	NA	39	39	39	39	39
Octene	NA	NA	49	NA	NA	NA	NA
Xylene	97	97	50	50	50	50	50
Pentane	200	200	200	200	200	200	200
Pentanol	NA	NA	35	35	35	35	35
Pentene	65	65	65	65	65	65	65
Pentene	65	65	65	65	65	65	65
Phenol	10	4.9	2.0	NA	NA	NA	NA
Phorone	NA	NA	19	NA	NA	NA	NA
Propane	490	490	490	490	490	490	490
Propanoic Acid	19	10	4.9	4.9	4.9	4.9	4.9
Propanol	NA	NA	39	39	39	39	39
Propanol	400	96	60	60	60	60	60
Propionaldehyde	NA	NA	39	39	39	39	39
Propyl acetate	250	200	40	40	40	40	40
Propylbenzene	NA	NA	10	NA	NA	NA	NA
Propyl chloride	NA	NA	29	29	29	29	29
Propylene	490	490	490	490	490	490	490
Propyne	250	250	250	250	250	250	250
Pyruvic acid	NA	NA	1	NA	NA	NA	NA
Styrene	98	50	10	10	10	10	10
Sulfur dioxide	3.8	1.9	0980	0.98	0.98	0.98	0.98
tert-Butyl alcohol	150	97	39	39	39	39	39
Tetrachloroethane	200	49	4.9	1.2	0.2	0.1	0.058
Tetradecane	50	50	50	50	50	50	50
Tetrafluoroethene	NA	NA	48	48	48	48	48
Tetrahydrofuran	250	200	40	NA	NA	NA	NA
Toluene	16	16	16	16	16	16	16
trans-1-Methyl-3-ethylcyclohexane	NA	NA	25	NA	NA	NA	NA
trans-1,2-Dimethylcyclohexane	26	26	26	26	26	26	26
trans-2-Butene	99	99	99	99	99	99	99
Trichloroethane	440	340	29	29	29	29	29
Trichloroethane	3.6	1.8	0.99	NA	NA	NA	NA
Trichloroethylene	49	11	9.2	3.7	1.8	0.92	0.46
Trimethylbenzene	50	25	3.0	3.0	3.0	3.0	3.0
Trimethylcyclohexane	NA	NA	24	NA	NA	NA	NA
Trimethylcyclohexane	NA	NA	68	NA	NA	NA	NA

Compound Name	1 hour	24 hour	7 days	30 days	180 days	365 days	600 days
Trimethylsilanol	160	19	11	11	11	11	11
Undecane	NA	NA	49	NA	NA	NA	NA
Valeraldehyde	96	48	30	30	30	30	30
Valeric acid	NA	NA	24	NA	NA	NA	NA
Vinyl chloride	130	29	1.2	1.2	1.2	1.2	1.2
Vinylidene chloride	5	2.5	2.0	0.50	0.082	0.037	0.022
Xylene	97	97	50	50	50	50	
Xylene	97	97	50	50	50	50	50